Structure and phase composition features of nickel-based superalloy after electron beam additive process

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Abstract. In the present work, the structure and properties of products from heat-resistant nickel-based superalloy ZhS6U formed by wire-feed electron beam additive technology were investigated. Products were obtained under different parameters of electron beam additive process (accelerating voltage, beam current and movement speed of working table were varied). It was shown that a high speed of displacement leads to the formation of defects in the form of cracks and delamination of the obtained product from the substrate, which also leads to the appearance of cracks. It has been established that the greatest energy input leads to evaporation of aluminum (the main hardening $\gamma$ phase). The phase composition of the additive product did not differ from the original material.

1. Introduction

Modern production of products and parts in various industries (aviation, space, energy, automotive, medicine) requires not only high-quality products, but also their economically profitable formation. In order to optimize the production process of critical products, they try to reduce the time of the technological process, the number of its stages and the volume of waste material. From this point of view, additive technologies are an attractive substitute for traditional production. Additive manufacturing consists of layer-by-layer formation of a product from a powder or wire raw material by melting it with a thermal source (electron beam, laser beam or electric arc). Modern additive technologies allow obtaining metal products from all kinds of materials, in particular from heat-resistant superalloys (alloys based on nickel, cobalt and some steels) [1, 2]. As known, such superalloys have increased values of long-term strength, as well as resistance to high-temperature corrosion and creep [3, 4]. Due to their properties, heat resistant superalloys have found application in the production of elements of gas turbine engines and plants [3, 4]. Traditionally, these products are produced by directional solidification technology based on the Bridgeman-Stockbarger method, which consists in the slow movement of the mold with the melt from the heating zone to the cooling zone. Currently, the cooling zone can be represented by the melt of an easy-fusible material (aluminum or tin) [5, 6]. Increasing the efficiency of heat removal leads to higher temperature gradients that promote directional growth of the crystallizing material structures. This approach tries to conduct the entire process of product formation at the lowest possible solidification rates, since there is a probability of temperature gradients radial components nucleation.
In the process of additive manufacturing there is a local melting of the fed material, this leads to the formation of a small molten pool. Due to the local nature of the melting and solidification processes, significant temperature gradients arise due to heat removal by thermal conduction into the work table and due to heat radiation into the walls of the vacuum chamber. It is worth noting that the formation of the N layer results in all-round heat dissipation, however, during subsequent application of the N+1 layer, the N layer is remelted repeatedly and during its solidification the radiation component of heat dissipation is significantly reduced. This leads to a unidirectional temperature gradient in the re-melted layers [7].

These features of the additive process are used in the healing of defects in products obtained by traditional directional solidification technology, as well as in the formation of products on single-crystalline substrates, in order to obtain similar structures in the final product [8, 9]. One of the technological features of additive manufacturing is the need to remove the substrate on which the product was formed. Because of this, the use of single-crystalline substrates significantly increases the cost of the final product. To avoid this, present work used isostructural material as a substrate, namely, austenitic steel, on which the product was formed from a heat-resistant nickel alloy.

2. Material and methods
The formation of the product was carried out using the wire-feed electron beam additive manufacturing facility developed in the Institute of Strength Physics and Materials Science of the Siberian Branch of the Russian Academy of Sciences [10]. From the initial material - ingot of ZhS6U alloy (chemical composition is presented in Table 1), rods were cut with an electric erosion machine. After removal of erosion products, purified bars were loaded into a special feeder of electron-beam setup [7]. By feeding the rods into the focus of the electron beam and moving the working table, layer-by-layer formation of the product in the form of a wall on a substrate of SS321 steel (chemical composition is presented in Table 2) took place.

| Table 1. Chemical composition (% wt.) of superalloy ZhS6U |
|-----------------|--------|---------|--------|--------|-------|--------|--------|
| W               | Ni     | Al      | Co     | Cr     | Mo    | Nb     | Ti     |
| 9.5-11.0        | Balance| 5.1-6   | 9-10.5 | 8-9.5  | 1.2-2.4| 0.8-1.2| 2-2.9  |

| Table 2. Chemical composition (% wt.) of SS321 |
|-----------------|--------|--------|--------|-------|--------|--------|
| C               | Mn     | Si     | P      | S     | Cr     | Ni     | Fe     |
| 0.08            | 2.00   | 0.75   | 0.045  | 0.030 | 17.0-19.0| 9.0-12.0| Balance|

During additive formation of the product, the following parameters were varied: accelerating voltage and beam current, speed of working table movement, strategy of electron beam movement (sample numbers and corresponding technological parameters are presented in Table 3). It is worth noting that unidirectional printing was used for printing all the products, except for product #5. In item #5, each time a new layer was deposited, the printing direction was reversed. In addition, a dynamic change in beam current was used in product #6 (unlike all other products), that is, the beam current varied during the formation of each additive product layers.

| Table 3. Parameters of wire-feed electron beam additive process |
|-----------------|--------------|--------------|----------|----------|---------|
| Product #       | Accelerating voltage (kV) | Current beam (mA) | Work-table movement velocity (mm/min) | Dimensions (mm) | Layers number |
| 1               | 25           | 45-36        | 180      | 20 x 65  | 16      |
| 2               | 30           | 60-47        | 250      | 10 x 70  | 12      |
The formed products were inspected for external macro-defects, and then templates were cut from which longitudinal (parallel to the 3-D printing trajectory) thin sections were prepared for metallographic studies. The grounded and polished samples were chemically etched with Marble reagent (50 ml HCl + 10 g CuSO₄ + 50 ml H₂O) and examined with an optical microscope AXIOVERT-200MAT (Zeiss) and a scanning electron microscope LEO EVO 50 (Zeiss). For finer structural studies and phase composition identification, a JEOL JEM-2100 transmission electron microscope (Tokyo Boeki Ltd.) was used. To prepare thin foils a 1051 TEM Mill (Fischione instruments) double-beam ion machine was used. X-ray studies were performed on a DRON-07 X-ray diffractometer (Burevestnik). Mechanical tests were performed on a UTS 1100M-100 1-U testing machine (Testsystems).

3. Results and discussion
Figure 1 shows images of the products obtained by the wire-feed electron beam additive technology. As can be seen from the above images in the process of technological parameters optimization the products were obtained with some macro defects: crack formation (products #1 and #2); delamination of the formed product from the substrate (product #2); excessive spreading of molten material (product #3); violation of geometry (products #4 and #5). The parameters for which item #6 was produced were chosen as the most optimal ones, since item #6 did not contain the above defects.

Figure 1. General view of products obtained by wire-feed electron beam additive technology; a) – product #1; b) - product #2; c) - product #3; d) - product #4; e) - product #5; f) - product #6.
The following peculiarities were revealed by detailed studies of the structure by optical and scanning electron microscopy methods. The structure of all products is represented by colonies of dendrites growing epitaxially in the direction of additive growth with an inclination towards the electron beam movement (except for product #5, where the inclination changed during formation of each new layer due to changes in the direction of the working table movement). The main structural-phase components of the nickel-based superalloy are the dendrite arms, the interdendrite space in which secondary phases are distributed: $\gamma/\gamma'$ - eutectic carbides like MeC (where Me is titanium, niobium and tungsten), Me$_6$C (where Me is chromium, molybdenum and tungsten). The integral chemical composition determined by X-ray fluorescence analysis of the products corresponded to the initial material (except for products #4 and 5). In items #4 and #5, a lower aluminum content (up to 1-2%) was observed due to aluminum evaporation due to increased heat input. This drawback was eliminated in item #6 by reducing the beam current. It is worth noting that when comparing the initial material in the cast state and after the additive process, a significant reduction in both dendritic arms (the primary dendrite arms spacing decreases from hundreds to tens of micrometers) and carbides is observed, and eutectic pools almost disappear in the additive material. In addition, in the cast material, carbides may also be present in the dendrite arms, what is not observed in the additive material. It is also worth noting that periodic thermal exposure and repeated remelting of the material during additive product formation does not lead to the formation of undesirable topologically closed packed (TCP) phases. This is confirmed by energy dispersive analysis and decoding of microdiffraction patterns obtained in the course of the TEM study.

Another material feature of additive nickel-based superalloy products is the presence of a structural gradient (Figure 2). And this feature is observed both in the direction of additive growing and in the direction of the worktable movement. Thus, the structure of the material changes from planar (i.e., it is impossible to distinguish any structural element; this area is usually preserved for several tens of micrometers) along the height of the product. Then a cellular structure is formed (closely spaced arms of dendrites of the first order; this area persists for hundreds of micrometers). Dendrites with arms of the second order appear next (this is the basic structure of all additive products). Finally, in the last layers a structure close to equiaxial or strictly horizontal growth of dendrites is formed (depending on the selected parameters of the additive process or heat input). Considering the structural changes along the direction of motion of the working table, it is clear that the structural features are observed only in the edge regions (at the beginning of the formation of each layer and at the end). At the beginning of the formed layer, strictly vertical growth of dendrites is observed, and at the end, the slope of the primary dendrite arms increases anti-parallel to the direction of motion of the working table, reaching values of 60 degrees from vertical to the substrate, depending on the feed rate of the working table.
Figure 2. SEM images of nickel-based superalloy structure after electron beam additive process; a) – planar and cellular structure; b) - dendrites with the second order arms; c) - lack of directional growth at last layer.

The features of the additive material structure described above are due to the fact that the most effective heat removal occurs at the interface with the substrate, and then the value of the temperature gradient gradually decreases, but its clear direction through the substrate to the worktable is preserved. This is reflected in the preservation of directional growth of the structures. The changes in the structure near the surface are caused by the increasing contribution of radiative all-round heat dissipation (these mechanisms are discussed in detail in [7]).

Since all the heat-resistant nickel-based superalloy products were formed on steel substrates, it is necessary to evaluate their influence. The SEM studies showed that in item #1 the substrate material is detected during the first 8 mm from the substrate. To minimize the effect of the substrate material, we increased the heat input (from 0.4 to 2.25 kJ/mm) by increasing the accelerating voltage (from 25 to 30 kV) and reducing the movement speed of the worktable (from 180 to 20 mm/min). This resulted in the fact that, in item #6, the chemical elements of the steel substrate were not detected in the product material at a distance of more than 3 mm from the substrate.

It is known that in the process of rolling steel a pronounced texture appears [11], the family of crystallographic planes {110} prevails in the plane perpendicular to additive growing. Since when forming additive products on single-crystal substrates, the crystallographic direction of the substrate [001] should coincide with the direction of additive growth, the crystallographic influence of the steel substrate should be evaluated. X-ray diffraction analysis revealed that a family of crystallographic planes {001} prevails along the direction of dendritic colony growth, which allows us to speak of the absence of crystallographic influence of the substrate on the additively formed product.

Based on the data obtained on the presence of defects, structure and phase composition, it was found that the parameters of the additive process by which the product #6 was obtained were optimal. Further, mechanical tests were carried out by static tension of the specimens. The test specimens were cut along the direction of additive growth (specimen #1) and along the direction of dendrite growth (specimen #2), and samples were also cut from the ingot of the original material (specimen #3). The results obtained during mechanical tests are presented in Table 4. According to the tests carried out, the mechanical properties of the additive product do not depend significantly on the chosen direction (especially taking into account the error). It can be said unambiguously that the achieved properties are superior to those of the original cast material. Thus, the ultimate strength increased by 12-20%, the relative elongation by 3-11%, the relative elongation increased by 4.5 times.

Table 4. Mechanical properties of the product of ZhS6U superalloy formed by wire-feed electron-beam additive technology

| Sample # | \(\sigma_u\) (MPa) | \(\sigma_{0.2}\) (MPa) | \(\delta\) (\%) |
|----------|-------------------|----------------------|-------------|
| 1        | 1209.5±9.2        | 1017.5±20.5          | 14.54±1.8   |
4. Conclusions
In this work, the authors obtained products from the nickel-based heat-resistant superalloy ZhS6U on steel substrates by wire-feed electron beam additive technology. Optimization of technological parameters of the additive process made it possible to obtain defect-free products. The structure of the material is represented by colonies of dendrites with a pronounced growth direction. The peculiarities of additive manufacturing do not lead to the formation of TCP phases. The presence of structural differences in the volume of the formed product and in the near-surface regions can be removed during minor mechanical post-processing. The austenitic steel substrate has no crystallographic effect on the additively grown product, and the minimization of the added material is achieved by increasing the heat input. The mechanical properties of the product obtained by the electron beam additive technology are superior to those of the original cast material. By reducing the number of process steps and by eliminating the need to prepare a casting mold for each new product, additive technology can accelerate the production of heat-resistant alloy products. However, in this case, additional operations were required to prepare the initial rods. Based on this, it can be assumed that additive manufacturing is comparable in cost to casting production, but produces products with superior properties.

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| 2 | 1195.5±37.5 | 968±4.2 | 12.1±1.3 |
| 3 | 1030 | 932 | 3.0 |