Investigation of the intermetallic coating of the Ni-Fe system obtained by surface laser treatment on a steel substrate.

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Abstract. The article presents the results of a study of the Ni-Fe system coating on a 09G2S (Fe-Mn9% Si2%) steel substrate obtained by laser surface treatment. The coating was obtained in two stages. At the first stage, a precursor coating (PC) of Nickel was applied by cold spray (CS). At the second stage, its surface was laser treatment. The article shows changes in the composition and properties of the coating after laser treatment at different thicknesses of the precursor coating and different laser treatment modes. The results of the study showed that the composition and structure of the coating can be controlled by controlling the thickness of the precursor coating, the scanning speed, the scanning hatch, and the number of repeated scans.

1. Introduction

One of the most common structural materials is steel. There are many different grades of steel that differ in alloying additives. In turn, alloying components provide functional properties, such as strength, corrosion resistance, radiation resistance, etc. [1-3]. Often steel with high strength has low corrosion resistance. At the same time, due to the need to introduce alloying additives, the cost of steel materials increases. It is known that it is possible to increase the corrosion properties of steel by using protective coatings. There are a large number of coatings that can significantly improve the surface properties of materials operating under extreme operating conditions [4, 5]. The most common are electrochemical methods for applying protective oxide coatings that are similar in properties to structural ceramics [6-8]. However, traditionally used coatings also have disadvantages, the most vulnerable zone is the boundary with the base metal. It is necessary to provide the best bond with the substrate (adhesive bond). This connection is provided by the use of laser cladding. The best adhesion can be obtained when the chemical composition of the coating is close to that of the substrate. This can be realized with significant alloying of the base material in a thin layer, for example, the introduction of nickel, chromium or aluminum into the composition of low-alloy steel can significantly increase the corrosion-resistant properties. This solution will allow the use of inexpensive, durable steel in corrosive conditions. This paper presents a method for surface alloying using a pre-deposited precursor coating layer. Due to the melting of the precursor coating on the surface of the substrate and the surface layer of the substrate using the power of a laser beam, the resulting coating has a number of advantages: compact microstructure, thickness control over a wide range. In addition, the coating can be designed under conditions of a nonequilibrium thermodynamic process. In recent years, references are often found in the literature on obtaining an intermetallic coating using laser radiation [9-12]. The aim of this work is to analyze the modes of laser processing such as during the formation of a corrosion-resistant Ni-Fe coating in situ using nickel powder deposited on a substrate of low-alloy steel 09G2S (Fe-Mn9% Si2%), depending on the processing modes and the thickness of the precursor coating.
2. Materials and equipment

2.1 Materials
Nickel powder produced by JSC Polema grade (Figure 1 and 2) with the addition of corundum with a fraction of ~ 20 μm was used as a starting powder material, which is a technological additive to ensure the stability of the coating process.

Sheets of 09G2S steel were used as a substrate. The size of the substrates was 50 × 25 × 6 mm.

![Figure 1. EDS Results of Nickel Powder](image1)

![Figure 2. The results of particle size analysis of nickel powder](image2)

2.1 Equipment
Technological and analytical equipment was used to study powder materials and obtain functional coatings:
«Dimet-403» – for applying a precursor coating by cold gas-dynamic spraying (Cold Spray CS);
Complex «Factory» – Laser Surface Treatment (LST);
Malvern Mastersizer 2000 – for determining the particle size distribution of powders;
Leica DM-2500 – optical microscope for metallographic research;
Tescan VEGA 3 – scanning electron microscope for metallographic research;
Tescan VEGA II – for the study of EPS microanalysis (X-ray microanalysis) of the elemental composition of powders and functional coatings;
Rigaku Ultima IV – for the study of X-ray structural analysis;
Nanoscan 3D – measurement of mechanical properties by the method of instrumental indentation in accordance with ISO 14577-1:2015.

3. Obtaining coatings

3.1 Production of cold spray coatings
The CS method was used to obtain a precursor coating as the most promising, which is described in the work [13, 14]. This method allows the application of coatings from commercial powder materials as well as from powders obtained using additional processing [15] The main advantage of the CS is the absence of high temperatures during coating. This eliminates changes in the chemical and phase composition of the coating and substrate during deposition due to the low temperature of the particles during deposition. [16].

In this study, a precursor coating with a thickness of ~ 31, 50, 80 μm was applied to the substrates.

3.2 Laser Surface Treatment
The surface treatment of the the precursor coating was carried out according to the scheme shown in Figure 3. The laser power was 180 W. Processing was carried out in the air.
Table 1. Parameters of laser coating treatment

| LST mode | Research area | Thickness PC, μm | Hatch, μm | Number of LST scans |
|----------|---------------|------------------|-----------|---------------------|
| 1        | 1             | 31               | 200       | 2                   |
| 2        | 2             | 31               | 200       | 2                   |
| 2        | 3             | 80               | 200       | 2                   |
| 3        | 4             | 80               | 200       | 2                   |
| 4        | 5             | 50               | 100       | 3                   |
| 4        | 6             | 50               | 100       | 2                   |

Figure 3. Laser Surface Treatment scheme: 1 – laser beam, 2 – velocity vector, 3 – substrate, 4 – laser treated surface, 5 – laser path, 6 – scan width, 7 – hatch

During laser processing, various variable modes were used: scanning speed, scanning hatch, number of processing scans (repeated scanning with a laser of the same area). Laser processing parameters are presented in Table 1. The study of various modes allows one to get a broader understanding of the influence of modes in the LST process.

Figure 4 shows samples with PC and after LST. The marked research area 1-6 are the zones in which the coverage was tested.

![Figure 4](image)

Figure 4. Appearance of coated samples: a – precursor coating after CS; b, c – after LST. Research area 1-6 – study areas.

4. Investigation

The coverage survey was carried out in several areas noted above. The study of the chemical ad phase composition was carried out from the surface of the sample, as well as on a transverse section. In this case, the surface was investigated directly after LST, as well as after removing a thin surface layer containing oxide modifications. Cross-sectional analysis of the structure shows the penetration depth as well as the uniformity of the chemical composition over the coating thickness.

4.1 The results of studying the coating surface after LST.

The surface of the coating is represented by uniformly distributed longitudinal hills and valleys, which are the result of exposure to laser radiation. It should be noted that the step of the elevations corresponds to the step of the scan. Also, on the surface there are chaotically distributed drop-like accumulations of aluminum oxide. Figure 5 shows the results of chemical analysis of the surface after LST of the surface of the precursor coating after CS and after LST.

Table 2 shows the results of the chemical analysis of the surface directly after LST.
The results show that the chemical composition of the surface changed after the LST process. This is probably a consequence of the mixing of the precursor nickel coating and the iron substrate material in a thin melt layer. After the treatment, the oxygen and aluminum content on the surface increased. This will make it possible to identify the accumulation of oxides on the surface as a result of the melting of corundum from the powder and subsequent agglomeration in the form of drops upon cooling after exposure of the laser, as evidenced by a significant increase in their size from 20 μm to 300 μm. It should also be noted that with a decrease in the scanning step from 200 μm (research area 2 and 4) to 100 μm (research area 5 and 6) and additional repeated scanning of the surface from 2 (research area 6) to 3 times (research area 5), the oxygen content on the surface decreases, which may indicate the evaporation of aluminum oxide during laser exposure. This is realized due to a longer exposure of laser radiation, and therefore lead to an increase in the heat input because reducing the scanning step and repeated scanning of the surface.

To study the chemical and phase composition of the surface, a surface oxide layer with a thickness of about 5-10 μm was removed. The results of chemical analysis showed a significant decrease in the content of aluminum and oxygen in the coating composition, which indicates the absence of oxides in the coating, Figure 6 and Table 3.
Table 2. The chemical composition of the surface of the samples after CS and after LST, for the above research area 1-6

| Elem. | 1  | 2  | 3  | 4  | 5  | 6  |
|-------|----|----|----|----|----|----|
| Al    | 5.85 | 6.71 | 6.02 | 11.97 | 3.6 | 4.98 |
| Fe    | 1.16 | 49.97 | 1.36 | 18.1 | 63.3 | 59.56 |
| Ni    | 86.84 | 15.35 | 85.92 | 43.03 | 13.2 | 13.03 |
| O     | 5.56 | 24.06 | 5.98 | 24.61 | 17.3 | 19.26 |
| Si, Mn|    |    |    |    |    |    |

This fact is also confirmed by the results of XRD analysis, Figure 7. The results of XRD analysis show the presence of two main phases in the coating, namely the $\alpha$-Fe phase and the Fe$_3$Ni$_2$ intermetallic. No pure nickel phase was found in the coating. This indicates its complete transformation into the nickel-iron intermetallic.

![Figure 7. XRD analysis results for the research area 2,4,5,6](image)

Table 3. Chemical composition of the surface after LST, and removal of the oxide layer for the above research area 2,4,5,6

| Elem. | 2  | 4  | 5  | 6  |
|-------|----|----|----|----|
| Al    | 0.25 | 0.35 | 0.22 | 0.18 |
| Fe    | 71.59 | 27.1 | 79 | 78.2 |
| Ni    | 24.75 | 70.1 | 17.6 | 17.8 |
| O     | 2.05 | 1.94 | 1.96 | 2.57 |
| Si, Mn|    |    |    |    |

In the research area 5, the content of the intermetallic is the lowest. The highest content of the intermetallic is observed in zone 4, where there was the greatest PC thickness. It should be noted that with an increase in the heat input during processing, the content of the intermetallic phase decreases. This can be explained by longer exposure to high temperatures and, as a consequence, slower cooling. With slow cooling, the formation of equilibrium structures occurs.

4.2 Research of a cross section.

Optical microscopy was used to determine the layer thickness after CS and LST, the results are shown in figure 8. Figure 9 shows a map of the elements of the precursor coating and the result of its laser treatment. The image is taken in such a way that two areas are analyzed at once, before and after the LST. The structure of PC allows makes it possible to identify individual particles of the powder from which the coating was obtained, namely, Nickel and corundum particles. The structure of the coating after LST is characterized by a change in composition, greater thickness and uniformity, as well as the absence of corundum. The boundary with the substrate is easily identified.
To study the uniformity of the distribution of the chemical composition over the coating thickness, an analysis was performed in several sections from the surface to the substrate. Figure 10 shows the maps of the distribution of elements in the research area 2,4,5,6. For a more visual representation of the uniformity of the composition, it is sufficient to trace the content of one of the main elements, for example, Fe. The results of Fe distribution over the cross section of the coating are shown in Figure 11.

As a result of LST, a uniform coating is obtained in which no composition gradient is observed. Therefore, the duration of the layer in the molten state is sufficient for mixing. The corundum contained within the precursor coating after processing is not identified. During the formation of a liquid melt, corundum under the action of a laser rises to the surface of the melt pool and collecting into agglomerates. This can be seen in Figure 11 d, namely, there is a pronounced rise on the surface with a clear boundary, the chemical composition corresponds to corundum.

Determination of microhardness was carried out by the method of instrumental indentation at a load of 3 g, the results are shown in Figure 12-15 and Table 4. This method will make it possible to assess the
hardness at low values of load in relatively thin layers [17]. The measurement values and their distribution are shown directly only for the coating, heat-affected zone and the substrate itself. The microhardness values for the transition zone from the coating to the substrate are not indicated in this work.

**Figure 12.** Determination of microhardness of research area 2 by the method of instrumental indentation at a load of 3 g: a - arrangement of indents; b - results of EDS analysis after indentation.

**Figure 13.** Determination of microhardness of research area 6 by the method of instrumental indentation at a load of 3 g: a - arrangement of indents; b - results of EDS analysis after indentation.

**Figure 14.** Determination of microhardness of research area 4 by the method of instrumental indentation at a load of 3 g: a - arrangement of indents; b - results of EDS analysis after indentation.
Figure 15. Determination of microhardness of research area 5 by the method of instrumental indentation at a load of 3 g: a - arrangement of indents; b - results of EDS analysis after indentation.

Table 4. Microhardness values obtained by instrumental indentation at a load of 3 g

| Study area | Indent № | Average |
|------------|----------|---------|
| 2          | 1 2 3 7 8 11 12 15 - - - | H (GPa) 3.85 4.27 3.43 4.73 4.24 3.46 4.27 2.43 - - - 3.84 |
| 6          | 1 2 3 9 10 11 15 16 21 22 23 | H (GPa) 3.54 4.04 3.16 3.85 3.08 3.96 4.17 2.59 3.95 4.11 3.98 3.68 |
| 4          | 1 2 4 9 11 13 - - - - - - | H (GPa) 3.35 3.48 4.43 4.21 4.55 4.66 - - - - - - 4.11 |
| 5          | 11 12 13 14 15 16 17 18 19 20 - - | H (GPa) 5.98 5.83 5.67 6.19 6 6.09 5.81 6.07 6.2 5.77 - 5.96 |
| Substrate near boubdary |  | H (GPa) 4.15 |
| Substrate |  | H (GPa) 3.73 |

The presented results show that the coating (number 5) has the highest microhardness, in which the largest amount of the α-Fe phase is observed. The microhardness of the coating containing the greatest amount of nickel in its composition in the form of the Fe₃Ni₂ phase is slightly lower. In addition, an increase in microhardness in the heat-affected zone was noted, which is consistent with the results of the use of surface laser hardening.

5. Conclusions

- The use of an LST pre-deposited precursor layer makes it possible to obtain a thin alloy layer with a controlled chemical composition on the substrate surface. The composition is controlled by changing the thickness of the precursor coating and varying the processing modes.
- The use of CS for applying a precursor layer is a technologically advantageous operation, since it allows to obtain a layer of material of the required thickness on the surface of the substrate.
- The corundum contained in the precursor coating after LST precipitates on the coating surface in the form of agglomerates about 300 µm in size, while no corundum remains inside the coating.
- Increasing the exposure of the coating at high temperatures reduces the amount of intermetallic phase in its composition. This increases the microhardness.
- The use of laser processing provides an increase in the hardness of not only the coating, but also the heat-affected zone.
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6. References

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