Laser alloying of nanocrystalline coatings

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Abstract. A new method for obtaining high-entropy alloys in the near-surface layer of a metal substrate is proposed. As a metal base, steel containing impurities of chromium, nickel and titanium is used. An ion-plasma method is applied to this substrate with an AlFe0.43 alloy 15 microns thick. Then the resulting coating was irradiated with a laser. As a source of laser radiation, a neodymium-doped aluminum-garnet laser was used. The duration of the flash of the laser pumping lamps operating in the free-running mode was 2×10^{-3} s. The energy of the laser pulse was 1 J, the repetition rate of the laser pulses was controlled from 0.1 to 35 Hz. Elemental analysis showed the formation of high-entropic coating with high performance characteristics.

1. Introduction
Increasing the life of the work of machine parts and machines, increasing the reliability and durability of the tool is an urgent task of industrial production. For a tool with increased viscosity requirements, high strength is created only in the surface layers. Various functional coatings are applied for this purpose: ion-plasma, electric arc, magnetron sputtering and others. There are known methods of chemical-thermal treatment of metals: cementation, nitriding, nitrocarburization and other - diffusion saturation (doping) of the surface layer with nonmetals (C, N, B, Si ...) or metals (Cr, Al ...). Particularly promising is the direction associated with surface modification-laser alloying (see, reviews [1-4]).
The most widely used laser doping was various fillers and laser additives [3]. Metal powders are also used [5].

2. Statement of a problem
In contrast to the methods of doping considered in [1-5], we used laser alloying of finished nanocrystalline coatings. Coatings were applied to 12Cr18Ni10Ti steel when the cathodes AlFe0.43 were atomized by the ion-plasma method. As a source of laser radiation, a neodymium-doped aluminum-garnet laser was used. The duration of the flash of the laser pumping lamps operating in the free-running mode was 2×10^{-3} s. The energy of the laser pulse was 1 J, the repetition rate of the laser pulses was controlled from 0.1 to 35 Hz.
Electron microscopy was carried out using a scanning electron microscope MIRA 3 from TESCAN. X-ray energy dispersive microanalysis system X-Act (Oxford Instruments) allows to locally determine the elemental composition on the sample surface.

3. Theory
Let us consider the problem of the diffusion of atoms (ions) in an unbounded plate of thickness h. For simplicity and comparison, we confine ourselves to the stationary case. Then the diffusion equation (c is the concentration of atoms) will have the form:

\[
\frac{d}{dx} \left( D \frac{dc}{dx} \right) = 0
\] (1)
In the classical case, D=const, and in our case D=D_0 ((1-\alpha)/(\alpha+x)) [6]. Here, the size factor is denoted by \alpha=2\sigma\upsilon/RT (\sigma is the surface tension, \upsilon is the atomic volume, R is the gas constant, and T is the temperature.) Taking into account the size effect, equation (1) is reduced to the form:

\[
\frac{c}{x+\alpha} \frac{dx}{dx} = \frac{C_1}{D_0}
\]  

(2)

Here C_1 is the integration constant. The solution of equation (2) has the form:

\[
c(x) = \frac{C_1}{D_0} (x + \alpha \ln x) + C_2
\]  

(3)

If in (3) D_0=const, then we have a classical solution of the problem:

\[
c(x) = C_1 x + C_2
\]  

(4)

In contrast to the classical problem (4), the logarithmic term appears in equation (3). But the most important thing is that the distribution of the concentration of diffusing atoms depends on the material of the substrate. For x = 0, it is clear from (3) that the solution diverges. Therefore, the boundary conditions must be specified not at x = 0, but at x = \lambda_{dB} - the length of the de Broglie wave of electrons. Only in this case the classical diffusion equations make sense.

4. Results of the experiments and discussion

Figure 1 shows a 3D image of AlFe0.43 coatings obtained on an NT-206 atomic force microscope prior to irradiation (a) and after irradiation (b), and in Figure 2 - a SEM image.

![Figure 1. 3D image of the AlFe0.43 coating before irradiation (a) and after irradiation (b) ](image)
The elemental composition of the AlFe_{0.43} coating prior to irradiation and after irradiation is presented in Tables 1 and 2.

Table 1. Elemental composition of the AlFe_{0.43} coating before irradiation

| Element | Weight % |
|---------|----------|
| C K     | 7.30     |
| O K     | 5.46     |
| Al K    | 12.35    |
| Mn K    | 0.36     |
| Fe K    | 74.53    |
| Total   | 100.00   |

Table 2. Elemental composition of the AlFe_{0.43} coating after irradiation

| Element | Weight % |
|---------|----------|
| O K     | 11.05    |
| Al K    | 14.10    |
| Ti K    | 30.06    |
| Cr K    | 15.48    |
| Mn K    | 11.37    |
| Fe K    | 18.95    |
| Total   | 100.00   |

Table 3 shows the friction coefficients of AlFe_{0.43} samples paired with aluminum and copper in argon medium without laser treatment and after laser treatment. Table 4 shows the values of the Vickers microhardness (HV) of AlFe_{0.43} samples in argon medium without laser treatment and after laser treatment.

Table 3. Results of tribological studies of the AlFe_{0.43} coating obtained in argon

| Sample                          | Coefficient of friction |
|---------------------------------|-------------------------|
| AlFe_{0.43} without laser treatment | 0.327          | 0.282          |
AlFe$_{0.43}$ after laser treatment & 0.142 & 0.148 \\

| Sample                        | Test load, kg | Microhardness, HV |
|-------------------------------|---------------|-------------------|
| AlFe$_{0.43}$ without laser   | 0.025         | 196.8             |
| AlFe$_{0.43}$ after laser     | 0.025         | 453.2             |

Table 4. The results of microhardness studies of the coating AlFe$_{0.43}$, obtained in argon

In the case of primary laser melting of a coated surface, the homogeneity of the layer is rather low (Fig. 2b). Repeated laser irradiation with milder modes ensures the production of high-quality doped layers and allows to reduce structural heterogeneity. In this case, the hardening particles consist of globular precipitates, which should not be the reason for the appearance of cracks during operation. Compared with the base metal, the layer is etched very poorly, which indicates its high corrosion resistance.

A comparison of the elemental composition before and after laser irradiation (Tables 1 and 2) shows that the coating composition has changed greatly due to mixing with the metal base particles. This is primarily due to the dependence of the diffusion coefficient on the composition of the metal substrate according to equation (3).

The resulting alloy is a highly entropic compound (Table 2), which contains at least 5 elements, the amount of each of them not exceeding 35 at.% And not less than 5 at.%. For such compounds, a large amount of entropy of mixing is characteristic.

In [7], highly-entropic alloys were synthesized for the first time, their name was proposed and it was shown that they could have a number of unique properties.

In work [8], the criteria for the formation of disordered solid substitution solutions in high-entropy alloys were analyzed. It is shown that no single criterion or a certain combination of them allows us to accurately predict the formation of solid solutions or intermetallide phases in highly entropy alloys.

Table 3 shows that the coefficient of friction decreases by more than 2 times. This is due to a decrease in the roughness of the laser coating reflow. The microhardness increases almost 3 times (Table 4), that is, the performance characteristics of the coatings are much better.

In [7], four main effects of high-entropy alloys are summarized, namely:

1. Thermodynamics: high entropy effect;
2. Kinetics: Sluggish diffusion;
3. Structure: strong lattice distortion;
4. Properties: cocktail effect. (1)

The condition for the thermodynamic stability of the phase is the minimum of its free energy. Since $G = U + H-TS$, high entropy leads to a decrease in Gibbs energy and stabilization of the solid solution.

2. The effect of sluggish diffusion follows from equation (3) and is related to the logarithmic term. Usually, this effect is used to explain the formation of nanosized precipitates, since in materials in which diffusion is difficult, embryos are easier to form, but grow slowly.

3. Since the dimensions of the atoms can be very different, the crystal lattice is highly distorted, which leads to high elastic stresses and inhibition of dislocations. This effect is confirmed by the superhigh strength of the bcc high-entropy alloys.

4. For metallic alloys, the cocktail effect indicates that unexpected properties can be obtained after mixing many elements that can not be obtained from any one independent metal. The effect of the cocktail shows that the properties of the alloy can be significantly altered by varying the composition and doping.

The widespread method of obtaining highly entropic alloys is arc melting. The temperature at arc melting can be very high (> 3000 °C). The technology of plasma spraying and laser or electron-beam surfacing is also used [8, 9]. Mechanical doping is also used, such as breaking in a ball mill and re-
welding the powder particles. By this method it is possible to synthesize equilibrium and nonequilibrium alloys, both by mixing elementary substances, and by dispersing the previously prepared alloys [9]. The method is used to produce dispersion-hardened nickel-based or iron-base alloys for the aerospace industry.

The resulting performance properties, as a rule, are not constant in time:
– can change spontaneously without the influence of external parameters, for example, as a result of natural aging, stress relaxation, creep, etc.;
– can be changed under the influence of external factors that arise during the operation of the part, for example, as a result of load, friction, corrosion.

The properties of the surface layer are also affected by the high oxygen content in the coating (Table 2). The rate of adsorption, as a rule, increases in time and occurs the faster the higher the temperature. The high temperature occurs with laser irradiation.

There is an opinion that initially an adsorption layer is formed, which later turns into an oxide layer. The first portions of oxygen are absorbed with the release of a significant amount of heat and, consequently, with a decrease in the isobaric potential, i.e. spontaneously. The thermal effect of oxygen adsorption has the same order of magnitude as the heat of formation of the oxide. Therefore, the adsorption of oxygen can be regarded as chemical.

5. Conclusion
The laser alloying method proposed in this paper differs from the works cited above [8, 9] in the simplicity of the design. This method has other advantages:
1) high wear resistance;
2) good antifriction characteristics;
3) high resistance to corrosion;
4) economy of coatings.

It is also shown that the structure of the surface layer plays an important role in the formation of highly entropic coatings.

It should be noted that the properties of the surface layer, that is, the structure and characteristics obtained by it due to the processing of the part, depend primarily on the forming technology and technology, which gives the surface special physicochemical and mechanical properties. In our case, this is laser treatment of the surface layer.

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