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Microstructure and mechanical properties of eutectic nickel alloy coatings

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Abstract. The paper discusses the peculiarities of a structure and a coating composition after reflow. It was established that the structure of coatings from nickel alloy is a solid solution based on nickel, the eutectic of γ-Ni+Ni3B composition and dispersed reinforcing particles. The content of alloying elements in the initial powder material determines the type of the coating structure and the formation of hypoeutectic or hypereutectic structures. The influence of formation conditions on the structure and physical-mechanical properties of the coatings is considered in this paper.

Key words: alloy, property, coating strength, hardness, structure.

1. Introduction

At present the plants both in Russia and abroad use alloys for the production of wear- and corrosion-resistant coatings by surfacing or spraying with subsequent melting. These alloys are characterised by: a relatively low melting point (950-1350 °C); efficient wetting of the surfaces of steels and other materials; dissolution of oxide films; the ability to form strong bonds with the substrate metal; high physico-mechanical and service properties, such as strength, hardness, wear resistance in the conditions of abrasive friction and friction with lubrication; chemical resistance in many media and atmospheres; antifriction properties; creep strength and etcetera.

This unique combination of properties of nickel alloys often makes them irreplaceable in protection and handling of components and equipment. Therefore, irrespective of the current large increase in the price of materials produced from nickel alloys, the application of these materials in reconditioning and hardening of expensive components is highly promising. Thus the problem of production of high-quality coatings requires urgent solution. The solution of this problem with special reference to specific components and materials has been treated in a large number of scientific and technical investigations, published in the last couple of decades. However, because of the multifactorial nature of the processes of spraying and surfacing with melting, the existence of a large variety of complicated compositions of materials of nickel alloys the coating formation has been studied insufficiently. In the present work, investigations were carried out into the effect of the main parameters of the process of melting materials produced from nickel alloys of the Ni- Cr-B-Si system (heating temperature and holding time) on the formation of the structure of coatings. In order to select the optimum melting conditions of coatings of different compositions, the experiments were carried out to determine the effect of temperature, time and rate parameters of heating on the structure and strength properties of the coatings and of the 'coating-steel base' composite. The significance of these investigations is conditioned by the difficulties in controlling the influence on the process parameters in the actual conditions of melting coatings on components.

The heating rate and temperature are very important in surfacing and in carrying out operations of melting of the coating. The process of melting by external heat sources (plasma and gas flame torches, laser and electron beams) is characterised by the supply of heat from the side of the surface of the coating. In order to avoid cracking, splashing, dripping and other negative phenomena, formed at high power, the rate and temperature of heating causing delamination and failure of the coatings, it is important to select the melting conditions for any type of treatment.

The holding period of the coatings at the melting temperature has a significant effect on the porosity of the coatings. In case of short period holding (several seconds), the residual porosity may exceed 10 %, especially in case of thick coatings (thicker than 1 mm). This is associated with high viscosity of the melt and inefficient degassing [1]. With an increase of the holding period in melting, the porosity decreases to 1-3 %. In addition to this, in case of rapid growth of the grains of the y-solid solution (up to 60 mm) and in long period holding (3-4 min), the hardness and strength greatly decrease (by 20-30 %). The short holding time makes it possible to fix the maximum dispersion of all structural components of the coatings. However, this is accompanied by extensive heterogeneity of the coating, inherited from the initial powder and the sprayed coating. Most importantly, by regulating the energy effect parameters of the heat source for a specific thickness and composition of the coating, it is necessary to ensure the uniform favourable distribution of temperature in the cross- section. In this case, it is possible to ensure suitable conditions for efficient penetration to the depth (without melting the hardening phases), maximum degassing and prevention of grain growth in the structure or, on the other hand, decrease in the dimensions and number of carbide and boride particles as a result of superheating when exceeding the optimum temperature in heating or the holding period, causing a decrease in the coating hardness.

2. Results and Discussion

In the initial condition, the powder materials of nickel alloys have a structure consisting of disperse grains of the solid solution based on nickel, a fine branched eutectic of the solid solution based on nickel Ni_3B, fine primary carbides of chromium and boron, and borides of nickel and chromium [2-7]. The results of investigations carried out in many studies show that after melting, the structure of the thermally sprayed coatings of nickel, like the structure of the materials of the powders, is represented mainly by the same four groups of the structural components. In many cases, the contradicting nature of the investigation results obtained by various authors in determination of the relationship of the main structural components in the coatings is associated with the factor that the phase and structural composition of the coating of a specific chemical composition depends on the degree of deviation of the coating from the equilibrium condition and the melting conditions (temperature, cooling rate and the cooling medium). The indeterminacy of the structural and phase composition results contradicts an understanding of the formation processes of the thermally sprayed coatings and the production of high-quality coating- substrate compositions. In this work, the investigations were carried out in order to determine the dependence of the volume fraction of the hardening phases on the melting temperature and the holding period at this temperature, and also on the content of alloying elements in the coating alloy. The conditions of coatings formation for producing a specific structure were varied by changing the melting conditions in a furnace, gas-flame, plasma, laser and electron beam methods. The results show that an increase in the content of alloying elements in the alloy increases the content of the eutectic and hardening phases and also the hardness of the gamma solid solution based on nickel as well as the hardness of the entire coating (Figure 1, Table 1). An increase in the content of the eutectic component in the coating is accompanied by a large increase in the hardness of the coating, with a simultaneous small decrease in strength (Figure 2). The volume content of the hardening phases and colonies of the eutectic in the alloys greatly increases after heating to the temperatures in the range of the solidus line of the Ni-Ni_3B system (Figure 3 and 4). At the same time, with an increase in the holding period at the melting point of the coatings, both in the furnace and in plasma heating and also in gas flame heating, the colonies of the eutectic rapidly grow with a relatively small growth of the particles of hardening phases (Figure 5 b)

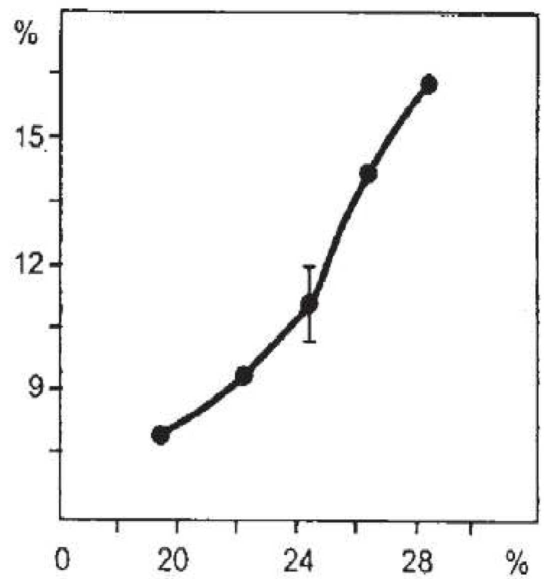

Figure 1. The dependens of the volume fraction of the hardening phases on the content of alloying elements in the coatings

In this work, the results of measurements of the structural parameters of coatings in melting are analysed.

The rate of growth of eutectic colonies and crystals of the carbide and borides is determined by the transformation temperature. In furnace heating, the melting of the coatings starts at the eutectic temperature and takes place in the equilibrium conditions, whereas in rapid heating with an increased heating rate, starting with gas flame, plasma heating and ending with laser and electron beam heating, it is necessary to heat the material to temperatures greatly higher than the eutectic temperature (100-300 °C).

It is well-known[5] that the main role in the formation and growth of the eutectic colonies and the growth of hardening phases is played by the diffusion processes taking place in the liquid phase between the sections of the melt, adjacent to the solid crystals, in our case - Ni_3B and the y-solid solution based on nickel.

Table 1. The content of alloying elements and structural components in the coatings

Coating	Content of allouing elements, %	Content of solid solution, %	Content of eutectic, %	Content of hardening phases, %	Hardness, HRC
PG-12N-01	12.5-23.6	50	43	7	35-40
PG-SR3	17.4-28.5	44	46	10	45
PG-12N-02	18.4-30.8	38	48	14	45-50
PG-10N-01	22.4-32.9	22	51	17	56-62
PG-10N-04	3.8-5.3	82	18	-	18-20

Therefore, the probability of formation of these excess phases and the extent of the eutectic reaction are determined by the degree of deviation of the heating temperature from the equilibrium conditions, the heating and cooling rate, and by supercooling of the alloy as well.

In most cases, melting of the majority of the alloys of the Ni-Cr-B-Si system during heating in the furnace is accompanied by the structure formation of the hypoeutectic of alloy type with the presence of primary phases of the gamma solid solution based on nickel, the presence of eutectic based on this solution and Ni_3B and precipitates of independent particles of Ni_3B and chromium carbides $Cr_{23}C_6$ and Cr_7C_3 (Figure 6 a, b).

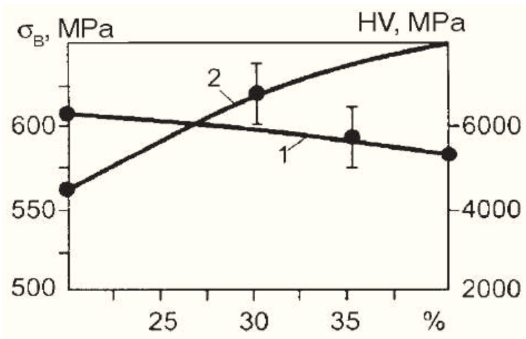

Figure 2. The dependens of the ultimate strength of (1) PG-10N-01-coating steel composite and (2) the hardness of the coating

In this case, depending on the heating temperature and time, as well as the cooling conditions, the resultant alloys may be characterised by the preferential content of a specific structural component of the coating. The formation of the eutectic takes place when the rate of its formation is higher than the rate of formation of the individual phases of the gamma solid solution and Ni_3B. Otherwise, the rapid process of formation of these separate phases does not make it possible for the eutectic colonies to grow.Increasing the heating temperature in the range of the solidus line of the alloys and the holding period at this temperature, the size of the eutectic colonies, formed during cooling, increases and the structure of these colonies may be characterised by a single developed formation penetrating through the entire volume of the coating and forming a unique frame (Figure 6c**).** This coating is characterised by high hardness and reduced plasticity. This is associated with the fact that the content of the Ni_3B hardening phase in the eutectic is very high and this phase controls the physical-mechanical and service properties of the coatings because the hardness of the eutectic is almost twice the hardness of the y-solid solution based on nickel. Therefore, the properties of the coatings strongly depend on the ratio of the structural components.

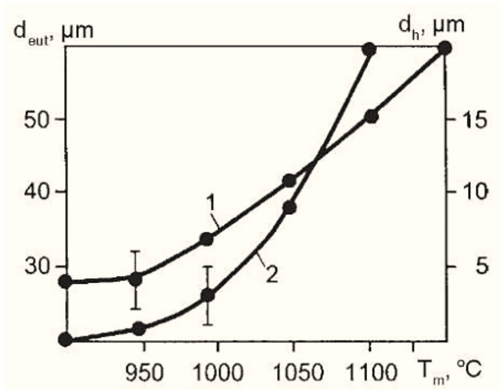

Figure 3. The effect temperature on the variation of the size of eutectic colonies (1) and hardening phases (2)

In the case of low degrees of supercooling, the examination showed the preferential fixing of the gamma solid solution based on nickel with the carbide and boride hardening phases distributed in the volume of the solid solution. In many cases, the alloys are characterised by the formation of a dendrite-like structure (y-solid solution based on nickel), penetrating through the entire coating (Figure 6d**).** In this case, the disperse eutectic (y-Ni + Ni_3B) fills the space between the dendrites. The material of this coating is characterised by relatively high strength and reduced hardness.

The process of crystallisation of the alloy of a specific composition with a high degree of supercooling is accompanied by almost complete suppression of the processes of formation of excess phases (y-solid solution based on nickel and Ni_3B), with the fixation of the eutectic (y-Ni + Ni_3B). The rate of formation of the eutectic for the melt of the given composition was higher. The large increase in the cooling rate of the coating-substrate composition using compressed air and a spraying device in a liquid results in the refining of the structure of the alloy of the coating but also causes an increase in the level of internal stresses and the probability of formation of microcracks. With the efficient application of powerful heating sources it is usually possible to produce structures with smaller grains in comparison to heating in the furnace, although the relationships of formation of the structural components remain unchanged. In this case, the structure of these alloys usually contains only a small amount of eutectic, with the formation of a protective structure with columnar grains of the gamma solid solution based on nickel. In the case of high cooling rates of compositions, a small content of the hardening phases is retained in the coatings.

The experimental results show that hardening of the coatings as a result of structure refining and efficient formation of a large amount of the eutectic and hardening phases, increases the wear existence of the alloys (Tables 2 and 3).

For this purpose, production tests were carried out on blades for cutting the wires of nonferrous metals, hardened with coatings on the cutting edge, and on punches for stamping foil. The durability of the blades and punches was determined by the operating time between two sharpening cycles (grinding). The experimental results obtained for the components with coatings produced by different methods and having different structures, were compared to the durability of the components produced from heat-treated Kh12F1 steel.

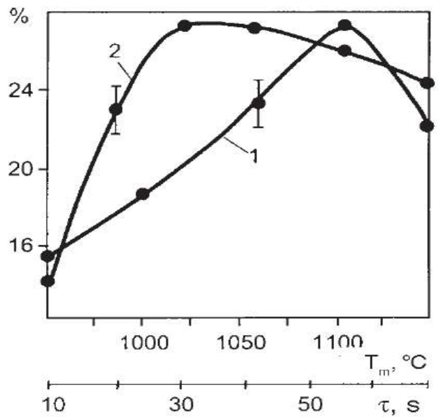

Figure 4. The dependence of the volume content of hardness in the PG-10N-01 coating on temperature (1) and the duration (2) of gas flame melting

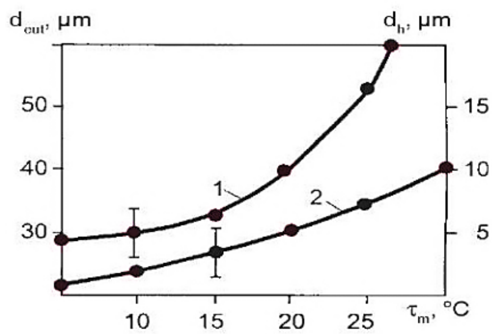

Figure 5. The dependens of the dimensions of eutectic colonies (1) and hardening phases (2) on holding time in gas flame melting

In the process of wire and foil cutting, the coating operates in the conditions of impact and abrasive loading, and the edges of the blades and punches are characterised by the formation of a nonuniform stress field, the nucleation and propagation of fatigue cracks and subsequent brittle failure and chipping, which are the main features of operation of these components. Therefore, the special features of service of these components determine the following most important technological properties: high hardness, strength, toughness and wear resistance. In addition, when selecting the material of the coating, one should take into account that the given coatings of the nickel alloys are characterised by their susceptibility to seizure, the capacity to polish during dry friction of the metal and by a low friction coefficient.

The analysis of the worn surfaces of the cutting edges shows that the wear of the coatings takes place due to damaging of soft components (initially the gamma solid solution based on nickel and, subsequently, the eutectic y-Ni + Ni_3B), exposure and subsequent chipping of hard carbide and borides phases (Figure 7a**).**

Therefore, the amount of hardening phases, the eutectic and the degree of hardening of the solid solution together determine the failure resistance of the coating material. The worn surfaces of the coating are characterised by the development of striations. During the wear of the coating with a more disperse structure and containing a large amount of eutectic and hardening particles (carbide and borides phases), the size and number of the striations on the surface decrease and the total wear rapidly decreases (Figure 7b**).**

Thus, the results of the tests carried out on the blades and punches show that the intensity and nature of wear of the coatings greatly depend on the type of the structure. Hardening of the coatings, obtained by means of refining the structure and purposeful formation of a large amount of the eutectic and hardening phases, increases the level of wear resistance.

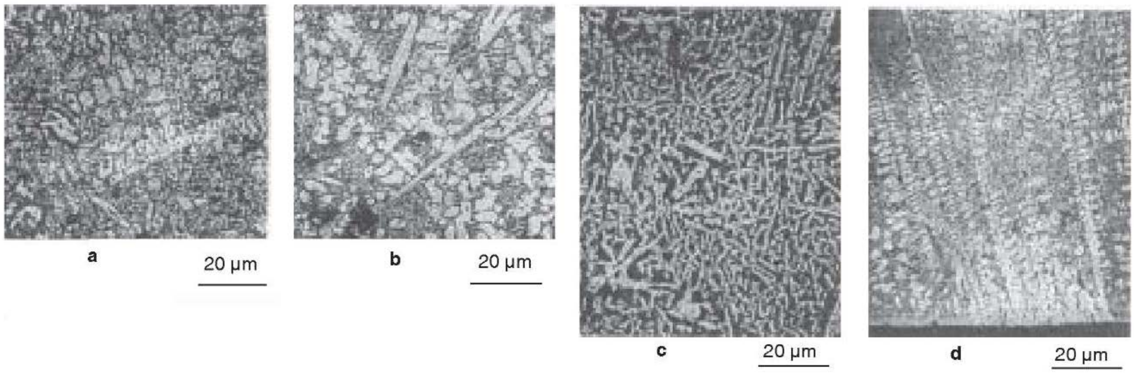

Figure 6. The structure of the coatings Ni-Cr-B-Si alloys after melting: a) preferential of the gamma Solid solution based on nickel and the γ-Ni+ Ni_3B eutectic; b) the high content of the carbide and boride hardening phases; c) eutectic frame; d) continuous dendritic structure

Table 2. Thermal processing of materials, their structure and properties

Materials of base and coating	Treatment	Structure	Hardness, HRC	Number of Shifts to regrinding	Hardness, HRC
Steel	Quenching and tempering	Martensit	54	12	83
PG-10N-01	Furnace	Eutectic	56	16	62
PG-10N-01	Gas-flame	Eutectic	58	18	56
PG-10N-01	Electron beam	Eutectic	60	23	43
PS-12N-VK	Gas-flame	Eutectic and carbides	62	25	40

Table 3. Thermal processing of materials, the structure and properties of the working edge

Materials of base and coating	Treatment	Hardness, HRC	Structure	Wear, μm	Number of shifts to regrinding
Steel	Quenching and tempering	54	Martensit	1.5	66
PG-10N-01	Furnace	56	Eutectic	1.4	71
PG-10N-01	Gas-flame	58	Eutectic	1.3	77
PG-10N-01	Plasma	54	Eutectic	1.7	58

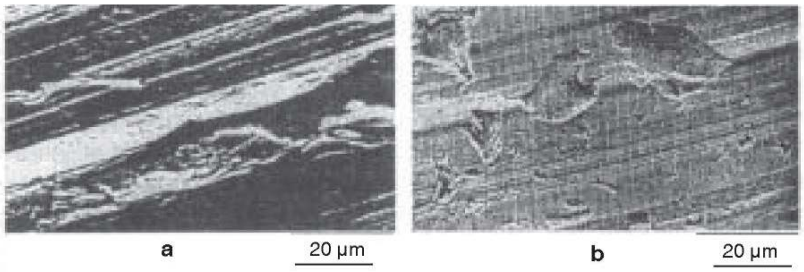

Figure 7. The worn surfaces of the coatings Ni-Cr-B-Si alloys PG-10N-01:
a) coarse structure; b) disperse structure.

3. Conclusions

The increase in the content of the alloying elements in the alloys from 12.5 to 32.9 % after melting in the furnace is accompanied by an increase in the volume fraction of the carbide and boride hardening phases from 7 to 17 %. The volume fraction of the Y-Ni+Ni$_3$B eutectic also increases from 43 to 51 %. An increase in the hardness of the coatings from 35 to 62 HRC accompanies this process as well.

The increase in the volume content of the Y-Ni + Ni$_3$B eutectic in the PG-10N-201 coating from 20 to 40 % increases its hardness from 563 to 650 MPa.

The increase in the temperature of gas flame melting by 50-200 °C above the solidus of the alloys and the increase in the holding period from 10 to 30 seconds result in the growth of both the amount of colonies of the Y-Ni+Ni$_3$B eutectic by 1.5-2 times and the volume content of the carbide and boride hardening phases. When heating coatings to higher temperatures and increasing the holding period, the hardening phases start to dissolve.

The wear resistance of the PG-10N-201 coatings increases by 1.3-1.9 times in case of the blades for wires cutting along with hardness increase of the content of the hardening phases and eutectic, whereas the wear resistance of the punches for foil cutting increases by 8-17 %.

The melting of the nickel alloy coatings is highly efficient in reconditioning and hardening of the components operating in the conditions of friction and impact-abrasive wear due to a two-time increase of wear resistance of the surfaces in comparison to the steel.

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