Prerequisites for obtaining wear-resistant metal coatings with a high-entropy structure by atmospheric plasma spraying, reflow, and hardening

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Abstract: The prerequisites for the use of atmospheric plasma spraying processes with multiple reflow and hardening of coatings are considered as a method of obtaining a highly entropic structure in them as applied to wear-resistant coatings.

1. Current state of research for multicomponent plasma coatings

In the last decade, the properties of a new class of multicomponent high-entropy alloys (HEA) have been actively studied in metal science. Active research in the field of multicomponent alloys, caused by additional interest due to the discovery of previously poorly studied compositions of alloying elements and substrates in equiatomic concentration, was started in the early 2000s in connection with the tasks of obtaining materials operating under extreme (elevated temperatures and loads) conditions, in particular, wear-resistant and heat-resistant alloys based on iron and nickel [1–2]. Such alloys consist of at least 5 basic elements in concentrations from 5% to 35% at. and have a high entropy of mixing, which can be considered as a measure of the probability of maintaining the state of their system [3]. This gives them advantages in comparison with traditional alloys in terms of physical and mechanical properties, thermal stability, resistance to corrosion and wear, and other properties [4]. The properties of such alloys depend on the chemical composition and method of preparation.

The available results of fundamental and experimental studies demonstrate the unique physical-mechanical properties of HEA, which can significantly expand the scope of modern metal materials [5]. The unique physical-mechanical properties of HEA led to the need for their use as coatings for various functional purposes.

For machine parts operating under friction and wear conditions, the urgent task was to obtain thermostable wear-resistant coatings from HEA. Parts that work under conditions of erosion and wear at high temperatures include parts of gas distribution mechanisms and a cylinder-piston group, internal combustion engines (valves, cylinders), brake parts, details of rocket engines (parts of gas turbines).

The entire spectrum of such materials and their possible properties has not been disclosed [6], while the majority of HEA studies are focused on elucidating the dependences of the properties of alloys on their microstructural parameters, and only a little attention is paid to the complex scientific and technical problem of studying and developing new methods for producing HEA. Among these works should be attributed, first of all, the review [7].
The vast majority of works are devoted to the study of all-metal samples from HEA. In their regard, many researchers obtained excellent results, but the practical application of new materials is hampered by the high cost of obtaining them. A small part of the work is devoted to the study of the production of multicomponent coatings with high entropy (HEA coatings). Such coatings are suitable as functional coatings for machine parts operating under high and extreme loads. This applies primarily to wear-resistant coatings with a thickness of 1...3 mm. In this case, the parts can be made of traditional alloys, and it would be techno-economically feasible to apply HEA coatings on the friction surface using one of the progressive methods.

Until now, such coatings have been obtained mainly by expensive vacuum, ion-plasma methods, and above all, by magnetron sputtering and vacuum-arc spraying of chemical compounds of metals with nonmetals [8], as well as by mechanical and laser alloying [9]. The use of vacuum-free technologies would reduce the cost of obtaining such coatings and increase their productivity. These technologies include gas thermal technology and, above all, plasma spraying in an open atmosphere. However, such methods have not been studied, or insufficiently studied [10]. In this regard, it is of great scientific and practical interest to obtain wear-resistant HEA coatings by combined processes based on atmospheric plasma spraying.

2. Conditions for obtaining multicomponent coatings with high entropy

In operation, HEA coatings must ensure the stability of the specified properties in phase and structural composition over a wide range of conditions and, above all, high adhesion properties that ensure coating retention under high operating loads. Coating processes must be high performance, affordable and economical.

The development of the technology of creating HEA coatings is possible while ensuring uniform mixing and homogenization of the composition when coating is applied to achieve high mixing entropy and to obtain single-phase disordered substitution solid solutions in the limit. Moreover, the entropy of mixing is a necessary but not sufficient criterion for the formation of a single-phase solid solution [7]. For the thermodynamic stability of a solid solution, a high degree of solubility of the constituent elements in each other is necessary. In turn, this requires that any element of the alloy can be replaced by another element with close values of electronegativity and atomic size, while maintaining the total number of constituent elements [1]. The influence of enthalpy of mixing and nonconfigurational contributions of entropy to Gibbs free energy should also be taken into account [7]. Only with a certain elemental composition does a disordered solution form, the mixing entropy of which completely compensates for the influence of both positive and negative enthalpy values [7].

The disorder of elements with different atomic radii in a solid solution due to their different combinations leads to lattice distortions, which affects the structure and properties of alloys. Due to the high density of defects, HEA occupy an intermediate position between crystalline and amorphous alloys [11]. The high density of defects leads to a decrease in the thermal conductivity of the alloy, which is undesirable for antifriction materials of machine parts from the point of view of heat removal from the friction zone.

Due to the fact that the normalized value of the diffusion energy of elements in different matrices is much higher than in pure metals, the following procedure for changing the diffusion coefficients [12] has been established: HEA < stainless steel < pure metal.

The low values of the diffusion coefficient of atoms in a multicomponent alloy determine the strength at high temperature [13], the formation of nanostructures and nanoscale precipitates [14]. This, in turn, can contribute to stability and increase the wear resistance of the alloy.

In highly entropic alloys, mixing leads not only to substitutional solid solutions, but also to other ordered and disordered phases, which contribute to the properties of the HEA. First of all, this relates to the correlation relation between the elastic limit – hardness, and also the relation between the yield strength – ductility [7]. These ratios in comparison with other metal alloys show the best combination of strength and ductility. An increase in ductility can be a prerequisite for reducing the likelihood of friction on the surface during the wear of a microcrack network, and an increase in hardness can be a
prerequisite for an increase in the wear resistance of HEA. At the same time, highly entropic alloys with a BCC lattice have predominantly high strength and low ductility, while alloys with an FCC lattice have low strength and high ductility. Therefore, for high wear resistance, it is presumably advisable to provide BCC phases.

The task of obtaining a coating with uniform mixing and homogeneity of the alloy components involves the study of unknown mechanisms and patterns of coating formation, as well as the influence of its factors on the structural and phase parameters, physical-mechanical and tribotechnical properties of the coatings, which are the criteria for the HEA coatings.

Factors of the processes of obtaining HEA are parameters of the composition of the components (alloy elements) and their amount in the alloy; external environment, means, modes and frequency rate of thermal, thermo-mechanical and/or mechanical effects on the formed alloy, coordinate distribution and time dynamics of this effect.

Known processes for producing HEA in which these factors are realized are casting processes, mechanical alloying, laser cladding, magnetron sputtering, and self-propagating high-temperature synthesis.

The solution to the problems of obtaining plasma coatings 1–3 mm thick with a uniformly mixed homogeneous composition is similar to the process of casting samples as a kind of melting method.

3. Patterns of HEA formation during casting

Some results of studies of foundry production of ingots are presented in [1, 15–20] and, in particular, in works in which, before melting, preliminary mechanical alloying of components in the form of powder in a high-energy ball mill was used [7]. The main method for producing ingots from HEA is multiple melting in vacuum or in an inert medium to increase the uniformity of the chemical composition and control the cooling rates during crystallization.

It was shown in [17] that an effective factor in controlling the formed structure of an alloy is its crystallization rate, which significantly affects the mechanism of alloy decay. With a fivefold remelting of HEA AlCrFeCoNiCu and low cooling rates of 10 K⋅c⁻¹, a dendritic (BCC) and interdendritic (FCC) phases are formed. These phases undergo spinodal decomposition with the release of the cubic phases A₂, B₂, Li₂, which differ in elemental composition and morphology.

At a high quenching rate of 10⁶-10⁷ K⋅c⁻¹, followed by heat treatment, an ultrafine-grained structure without dendrites with the presence of a B2 nanodomain superstructure is formed. Upon subsequent thermal annealing, crystalline multicomponent cubic phases are formed in a small amount [18].

In a study of the evolution of HEA Al₅₀CoCrFeNi depending on the aging temperature (350–950 °C) [19], it is noted that the negative enthalpy of mixing of alloy elements with a high concentration of them promotes the formation of intermetallic compounds of nickel with aluminum, that is, ordered structures. An increase in the aging temperature leads to a decrease in the proportion of intermetallic compounds.

An increase in the concentration of certain elements also leads to the formation of intermetallic compounds. Thus, in [20], the formation of CoCr and Ti₂Ni intermetallic compounds in the dendritic phase of HEA Al₅₀CoCrCuFeNiTiₓ at x = 1.2 was found.

4. The effect of plastic deformation and heat treatment on HEA properties

Intense plastic deformation by comprehensive forging of HEA AlCrCuNiFECo results in improved strength characteristics [21]. In comparison with a cast alloy, the brittle-viscous transition decreases from 700–800 °C to 600–700 °C after forging. At temperatures above the temperature of the brittle-viscous transition, the softening of the forged alloy is more noticeable than cast. In this case, a brittle-viscous transition occurs at the same values of tensile strength (350 MPa) for both states. This can positively affect the wear resistance of the alloy with respect to preventing the formation of fatigue cracks on the friction surface of the alloy.
High temperature treatment is accompanied by a transition to a superplastic state. In this case, the cast alloy has a region of local deformation and fracture occurs with a small elongation. Forged alloy is deformed more uniformly without a neck and with a large elongation.

Annealing significantly affects the microstructure and properties of HEA. An increase in the annealing time at 700 °C changes the microstructure of HEA Al05CoCrCuFeNi from elongated dendrites to a polygranular structure [22]. The authors suggest that this is due to the formation of an intermetallic compound — the σ-phase, or solid solutions based on CrFe and CoCr. An increase in temperature to 900 °C leads to the formation of a fine-grained structure without rod-like secretions and elongated dendrites. Annealing at 1100 °C led to the formation of a phase composition similar to the composition of the samples after casting, but with a fine-grained structure.

Due to the weak diffusion in HEA, the cooling of the heated sample during annealing proceeds rapidly, which does not allow completion of the phase transformation with the formation of new phases.

Annealing of samples from HEA CoCrFeNiTiAlx leads to an increase in Vickers hardness [23]. The authors attribute this to an increase in intermetallic compounds having a higher hardness than traditional alloys, as well as the effect of solid solution hardening. Annealing for this alloy showed very high compressive strength (2.6 GPa) at x = 0.5 at room temperature and ductility (13%). A further increase in aluminum content reduces strength and ductility.

5. Prerequisites for obtaining multicomponent coatings with high entropy by processes based on atmospheric plasma spraying, reflow, and electromechanical processing

A review of the methods for producing highly entropic alloys based on the casting method, akin to the plasma spraying method with multiple fusion in an inert medium, allows us to draw some practical conclusions.

The maximum entropy of a multicomponent alloy is determined by the formation of a disordered single-phase substitutional solid solution, which is ensured primarily by the elemental composition. For this, it is necessary to take into account the influence of enthalpy of mixing and non-configurational contributions of entropy to the Gibbs free energy. Only with a certain elemental composition does a disordered solution form, the mixing entropy of which completely compensates for the influence of both positive and negative enthalpy values. For the thermodynamic stability of a solid solution, a high degree of solubility of the constituent elements in each other is necessary so that any element of the alloy can be replaced by another element with close values of electronegativity and atomic size, while maintaining the total number of constituent elements.

Due to the high density of defects, HEA occupy an intermediate position between crystalline and amorphous alloys. The high density of defects leads to a decrease in the thermal conductivity of the alloy, which is undesirable for antifriction materials of machine parts from the point of view of heat removal from the friction zone.

The normalized value of the energy of diffusion of elements in different matrices of HEA is much higher than in pure metals. Low values of the diffusion coefficient of atoms in a multicomponent alloy determine high strength at high temperatures, the formation of nanostructures and nanoscale precipitates. This, in turn, can contribute to stability and increase the wear resistance of the alloy.

The ratio of the elastic limit - hardness and the ratio of yield strength - ductility in comparison with other metal alloys show the best combination of strength and ductility. An increase in ductility can be a prerequisite for reducing the likelihood of friction on the surface during the wear of a microcrack network, and an increase in hardness can be a prerequisite for an increase in the wear resistance of HEA. At the same time, highly entropic alloys with a BCC lattice have predominantly high strength and low ductility, while alloys with an FCC lattice have low strength and high ductility. Therefore, for high wear resistance, it is presumably advisable to provide BCC phases.

An effective factor in the regulation of the formed alloy structure is its crystallization rate, which significantly affects the mechanism of alloy decay. The high quenching rate of 10⁶–10⁷ К∙с⁻¹ with subsequent heat treatment forms an ultrafine-grained structure without dendrites with the presence of a B2 nanodomain superstructure. Upon subsequent thermal annealing, crystalline multicomponent cubic
phases are formed in a small amount. Annealing significantly affects the microstructure and properties of HEA. For example, annealing of samples from HEA CoCrFeNiTiAl leads to an increase in Vickers hardness. Due to the weak diffusion in HEA, the cooling of the heated sample during annealing proceeds quickly, which does not allow to complete the phase transformation with the formation of new phases, which can be considered a positive factor in relation to the production of single-phase structures.

The negative enthalpy of mixing of alloy elements with their high concentration promotes the formation of intermetallic compounds, i.e., ordered structures. An increase in the aging temperature leads to a decrease in the proportion of intermetallic compounds. An increase in the concentration of certain elements also leads to the formation of intermetallic compounds.

Intensive plastic deformation by comprehensive forging, for example, HEA AlCrCuNiFeCo, leads to an improvement in strength characteristics, leads to a decrease in the temperature of the brittle-viscous transition. This can positively affect the wear resistance of the alloy with respect to preventing the formation of fatigue cracks on the friction surface of the alloy.

6. Conclusion

Known facts allow us to offer methodological recommendations for obtaining wear-resistant wind turbines-coatings by plasma spraying with multiple reflow:

– the use of multiple reflow in an inert environment;
– selection of the elemental composition of the alloy with high solubility of the constituent elements in each other and with close values of electronegativity and atomic size;
– for high wear resistance of the HEA coatings, it is presumably advisable to provide BCC phases;
– for the formation of an ultrafine structure without dendrites, it is necessary to provide a high cooling rate of up to $10^6-10^7$ K·s$^{-1}$ with subsequent heat treatment, which can increase the hardness of the coating;
– improving the strength characteristics and wear resistance, as well as preventing the formation of fatigue cracks on the friction surface can be obtained using intense plastic deformation. An effective way to do this is to electromechanically harden the coating.

Additional control parameters for producing HEA coatings are plasma spraying, reflow, and electromechanical processing of local and general effects in steady and dynamic modes with modulation of parameters [10, 24].

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