COLD SPRAY COATINGS OF Al–Fe–Cr ALLOY REINFORCED BY NANO-SIZED QUASICRYSTALLINE PARTICLES

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By using powders of high-temperature strength aluminum alloys such as $Al_{94}Fe_3Cr_3$ and $Al_{94}Fe_{2.5}Cr_{2.5}Ti_1$ which were fabricated by the water-atomized technique, the efficient application of the cold-spray process for the consolidation of metal particles by severe plastic deformation with retaining the quasicrystalline particles of nano- and submicroscaled sizes (<100 to 200 nm) in the deformation-induced structure is justified. A model for the plastic deformation of powder metallic particles under cold-spraying conditions is developed. The effect of plastic deformation characteristics on the structure and mechanical properties of coatings and a substrate is studied.

1. Introduction

The contemporary development of technique sets new requirements to the lightening of machine parts and mechanisms operating under extreme operation conditions. A particular place in the solution of this problem is occupied by protecting Al-based coatings, whose properties allow one to ensure the efficient protection of the surface of a base material against the negative influence of external factors such as, in particular, corrosion and erosion.

From this viewpoint, new potentialities are opened by light Al-based composites (in particular, alloys on the basis of Al–Fe–Cr system) reinforced by disperse particles of quasicrystalline phases [1–4]. The mentioned materials combine the high corrosion resistance inherent to Al alloys with the unique complex of mechanical properties, namely, the high strength held up to 573 K and the sufficient plasticity. Unfortunately, such materials have not been used for the fabrication of coatings up to now. In most cases, coatings are obtained by means of gas-thermal spraying (mainly by plasma or detonation spraying) of powders. However, due to high temperatures of a gas jet which can attain 5000 K and more, the use of the mentioned methods does not allow one to conserve metastable quasicrystalline phases in the structure of powders (in particular, in the Al–Fe–Cr crystal intermetallidic compounds during the heating [3]. Wide scopes for the fabrication of coatings with metastable quasicrystalline particles are opened by a new method of cold gas-dynamic spraying (CGDS). Due to the use of a Laval nozzle, this method allows one to attain supersonic velocities of powders at relatively low temperatures (from room one to 1000 K) [5].

The purpose of the present work is to study the applicability of the CGDS method as for the consolidation of the powders of Al alloys of the Al–Fe–Cr system with metastable quasicrystalline particles, as well as the effect of this method on the formation of a structure and mechanical properties of a coating material and the substrate.

2. Materials and Experimental Procedure

Coatings were sprayed by using the powders of $Al_{94}Fe_3Cr_3$ and $Al_{94}Fe_{2.5}Cr_{2.5}Ti_1$ alloys reinforced by disperse quasicrystalline particles with size ranged from 100 to 200 nm. By the data published in [3], the fraction volume of the quasicrystalline phase in a powder was about 30%. In the application of coatings by the CGDS technique, we used the powders of alloys with a size of particles less than 40 μm which were produced by the water-atomized technique according to the novel WAN process [6] when the pressure of water jets was 10 MPa under a temperature of 1573 K and pH = 3.5. The content of oxygen in the powders of $Al_{94}Fe_3Cr_3$ and $Al_{94}Fe_{2.5}Cr_{2.5}Ti_1$ alloys did not exceed 0.3 mass.%, which is close to the oxidation level of gas-atomized Al powder.

Coatings were applied in the air environment on a cold (293 K) substrate at a mass flow velocity ~800 m/s and a temperature of 473 K. Prior to the process, the substrate specimens made of a rolled strip of low-carbon steel St3 of 1.5–3.0 mm in thickness were subjected to the sandblast processing.

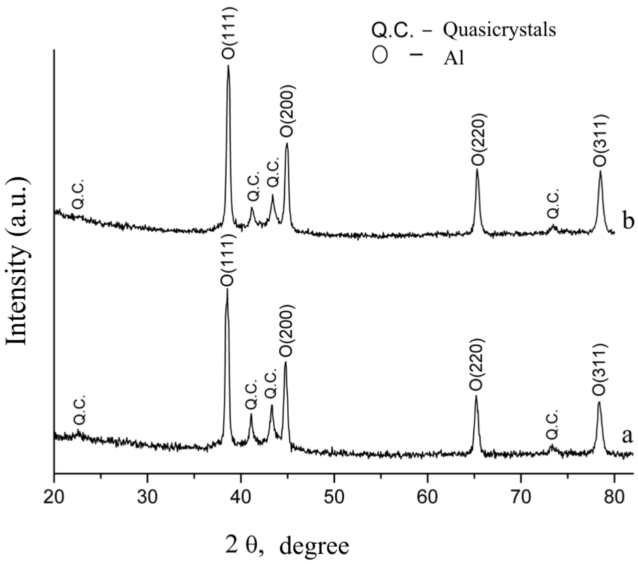


Fig. 1. X-ray diffraction patterns of $Al_{94}Fe_3Cr_3$ powder (*a*) and cold sprayed coatings obtained from it (*b*)

Structural characterization of coatings was performed by X-ray diffraction analysis and optical and scanning electron microscopies (SEM) on polished surfaces and in cross-sections of coatings. The aspect ratio of a powder particles (k_f) of Al alloy in coatings was determined by using SEM images and characterized by the ratio of the principal axes (the major axis to the minor one). The degree of deformation of the alloy was calculated by using the determined aspect ratio k_f of powder particles according to the accepted model of their interaction with the substrate.

The mechanical properties of coatings and the substrate were evaluated by the measurements of microhardness and plasticity characteristic δ_H which were determined under indentation according to the test method, whose procedure includes the protective measures aimed at the elimination of the effect of the scale factor on the results of measurements [7]. With regard for this method, we carried out the quantitative measurements of the above-mentioned mechanical characteristics of coatings and the substrate at the load $P = 0.1$ N.

The plasticity characteristic δ_H was calculated by the formula [8]

$$\delta_H = 1 - 14.3\ \left(1 - \nu - 2\nu^2\right) \frac{HV}{E}, \tag{1}$$

where E is the Young modulus of material, and ν is the Poisson's ratio.

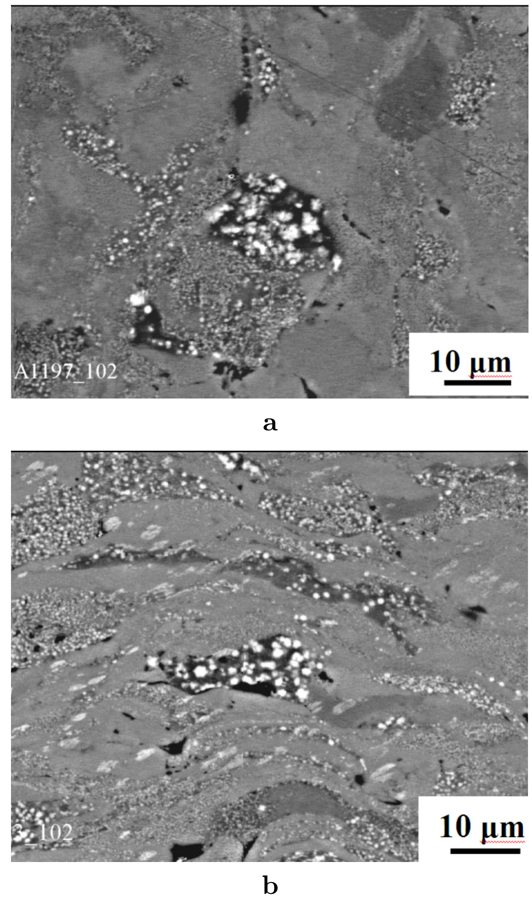


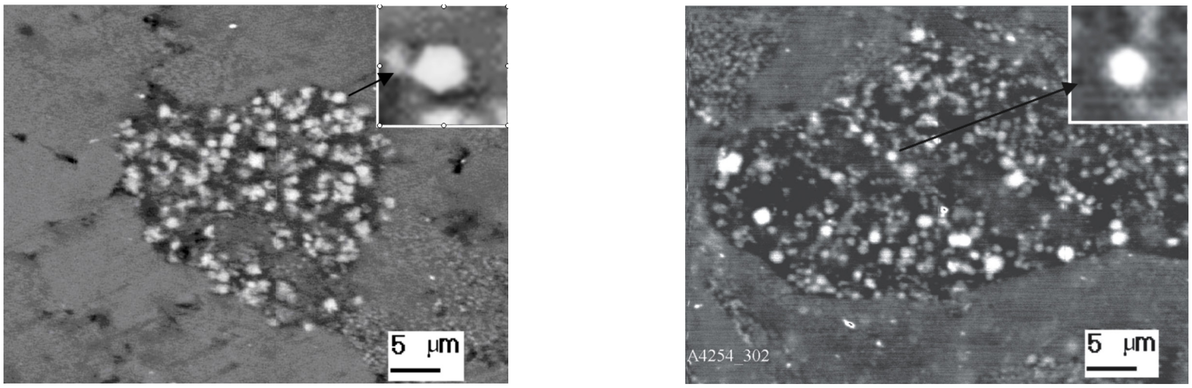
Fig. 2. SEM-image of the surface (*a*) and cross-section (*b*) of coating

3. Experimental Results

3.1. Structure of coatings

In the X-ray diffraction patterns of coatings, we recorded the reflexes of Al and quasicrystalline phases of $Al_{74}Fe_{12}Cr_{12.5}/Al_{74}Fe_{12}(CrTi)_{12.5}$ type [9], whose intensity was similar to that of the reflexes of the mentioned phases presented in the initial powders (Fig. 1).

It is essential that an irregular polyhedral shape of metal particles altered after the coatings deposition suggesting their severe plastic deformation (Fig. 2). In the cross-sections, particles of a powder have the elliptic shape with the aspect ratio $k_f \approx 4.7$. As distinct from this case, the morphology (shape and size) of disperse quasicrystalline particles was not changed as compared with that of the initial powders (Fig. 3). Because of different cooling conditions of powder particles in water jets, the sizes of quasicrystals in the individual metal



a **b**

Fig. 3. SEM-image of a particle of $Al_{94}Fe_3Cr_3$ alloy (*a*) and a coating obtained from it (*b*)

particles of coatings were found to be unequal, reaching 1.5 μm in some causes (Figs. 2 and 3). A certain amount of quasicrystalline particles has form of pentagonal "stars", by reflecting the rotation symmetry of the fifth order of the icosahedral *i*-phase, which is in a good agreement with the previously published data [3].

Observation of SEM-images of coatings showed the absence of a continuous oxide film at the coating–substrate interface, as well as at the boundaries between powder particles. This fact can be explained by that the impact of powder particles with a substrate and with one another occurs under high velocity ($\sim$800 m/s), which favors the fracture of the thin oxide film on particles surface due to severe plastic deformation (SPD). The interaction of juvenile surfaces of alloy particles allows the formation of a strong metallic bonding between them and good adhesion to the substrate. Residual porosity of coatings was believed to be not higher than 3%, no defects like cracks or delaminations were revealed.

3.2. Mechanical properties of coatings and a substrate

The results of the present study showed that the microhardness of coatings exceeds almost by twice the microhardness of the initial powders, although the values of the plasticity characteristic δ_H (Table) were found to be somewhat smaller.

It is worth noting that, despite higher microhardness, the values of the plasticity characteristic of δ_H for the coatings doped by Ti ($Al_{94}Fe_{2.5}Cr_{2.5}Ti_1$) did not differ from those of δ_H for a coating applied by using an alloy of the base composition ($Al_{94}Fe_3Cr_3$). The higher microhardness of a coating on the basis of $Al_{94}Fe_{2.5}Cr_{2.5}Ti_1$ alloy is accompanied by a higher Young modulus (Table), which can compensate the increase of HV as could be seen from (1) for the plasticity characteristic δ_H.

The value of plasticity characteristic δ_H for both types of coatings was determined at the level of 0.83, whereas this characteristic for the initial powder exceeded the critical value $\delta_H = 0.9$ (Table), implying plastic behavior of the alloy under standard used tests in tension and bending [8]. We may assume that just a high plasticity of alloys is the factor which clarifies the absence of the origination of cracks and delaminations during the spraying of coatings.

It was revealed that, while using the CGDS technique, the significant increase of the microhardness value for the Al-based coatings was accompanied by a significant hardening of the steel substrate at the distance from the interface as great as 0.6 mm. For example, the microhardness of a substrate area near the interface was increased by 50%, attaining the value of microhardness of the coating. The absence of changes in the morphology of the area above allows us to conclude

Mechanical properties of the initial powders and coatings obtained by the method of cold gas-dynamical spraying

Alloy	Young modulus, E (GPa)$^{1)}$	State of the alloy	Microhardness, HV (GPa)	Plasticity characteristics δ_H
$Al_{94}Fe_3Cr_3$	87.7	Powder	0.91±0.3	0.92
		Coating	1.95±0.12	0.83
$Al_{94}Fe_{2.5}Cr_{2.5}Ti_1$	89.8	Powder	1.03±0.3	0.91
		Coating	1.99±0.14	0.83

N o t e: $^{1)}$ values determined under conditions of the four-point bending of massive specimens produced by extrusion [2, 4].

that the mentioned increase of the microhardness occurs according to the dislocation mechanism.

4. Discussion of Results

By considering the fact that the obtained results testify the IPD of Al powder particles, it is expedient to estimate the degree and the rate of their deformation under CGDS conditions.

According to the ideas accepted in theory and practice of gas-thermal spraying, the consolidation of powder particles during the formation of coatings occurs under effect of impact pressure p_s, which deforms elastically only the frontal part of powder particles, and a head pressure p_f which causes a plastic deformation of particles [10]:

$$p_s = \frac{k_s}{2}\rho_p v_p V, \tag{2}$$

$$p_f = \rho_p V^2, \tag{3}$$

where k_s =2 is the stiffness for a rigid particle, ρ_p is the density of a particle which is approximately equal to 2.89×10^3 kg·m^{-3} for the alloys under study, $v_p = 5.08 \times 10^3$ m/s is the sound velocity in Al, and $V = 800$ m/s is the mass flow velocity.

The results of calculations indicate that the impact pressure p_s is about 14.7 GPa, which is higher by one order of magnitude as compared to the head pressure p_f = 1.9 GPa. However, the operation time of these pressure components strongly differ from each other [10]. Namely, the operation time of the impact pressure p_s (10^{-11}–10^{-9} s) is less by four orders as compared to that of the head pressure p_f (10^{-7}–10^{-5} s). In view of this fact, we used $p_f = 1.9$ GPa in the following calculations.

In order to evaluate the degree of deformation (ε_e) for particles of Al alloy in the CGDS process, we accepted a simplified scheme for alteration particle morphology from the initial powder to that revealed in coatings (Fig. 5). We assumed that powder particles have spherical shape with diameter D_0 and volume V_{sp} (Fig. 5,*a*). To facilitate the evaluating calculations, we approximated the shape of initial powder particles by a cylinder (Fig. 5,*b*) with the height $H_0 = D_0$ and volume ($V_i = V_{sp} = \frac{1}{6}\pi D_0^3$) to be the same as that for a spherical particle. According to the accepted conditions of approximation, the diameter of the base of a cylindricalparticle (D_i) has to be $D_i = 0.82D_0$.

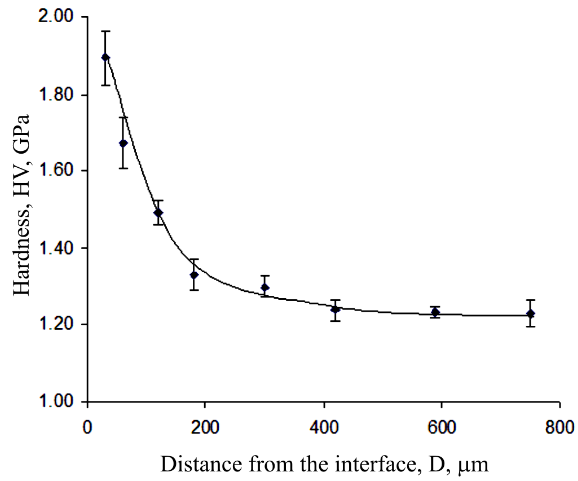


Fig. 4. Distribution of the microhardness in the transient zone of a steel substrate positioned on the boundary with a coating

Oblate powder particles belonging to the structure of coatings were also approximated by a cylinder (Fig. 5,*c*). The major axis of the elliptic particle in coating was taken as the base diameter ($D_f > D_j$), and the cylinder height was determined with regard for the experimental value of the aspect ratio of a particle k_f as $H_f = D_f/k_f$.

Since the volume of a deformed powder particle is constant under a deformation ($V_f = V_i = V_{sp}$), it is easy to show with regard to its geometric sizes that the base diameter of a deformed cylinder (D_f) depends on the diameter of the initial spherical particle in the following manner: $D_f = \frac{1}{6}\pi D_0^3 \frac{\pi D_f^2}{4} k_f \approx 0.87\sqrt[3]{k_f D_0}$.

In view of changes in the shape of a powder particle under its impact with the substrate (or with the previously deposited particle), the degree of its deformation can be given by the formula

$$\varepsilon_c = \frac{S_f}{S_i} - 1 = \frac{D_f^2}{D_i^2} - 1 = \frac{(0.87k_f D_0)^2}{(0.82D_0)^2} - 1 \approx 2.17, \tag{4}$$

where $k_f = 4.7$ is the aspect ratio of a deformed particle. Thus, the true deformation (e_c) of a powder particle during the spraying of a coating can be estimated as $e_c = \ln(1+\varepsilon_c) \approx 1.15$.

It is essential that the true degree of deformation (e_c) of powder particles during the consolidation in a coating is almost by twice less than that of powder particles of the same alloys under their consolidation by the extrusion technique (e_e = 2.28) [4]. At the same time, by possessing the twice higher microhardness than that of initial powders, the coatings demonstrate higher

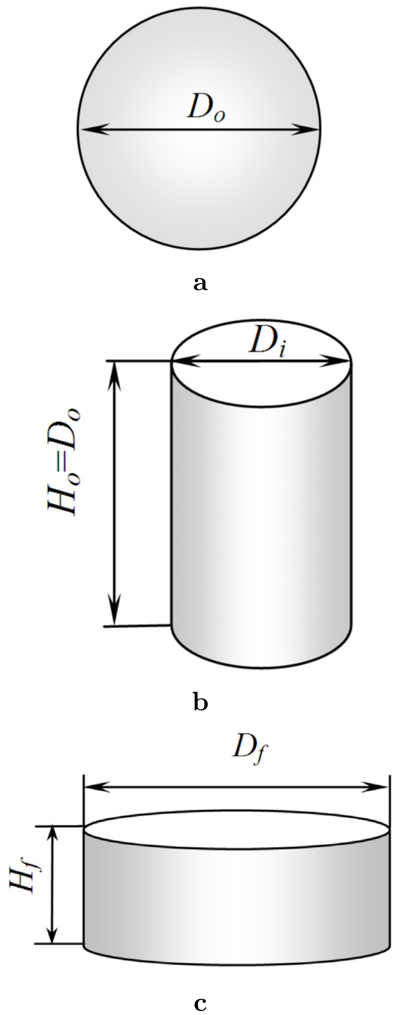


Fig. 5. Scheme of the deformation of a metal particle under the action of a head pressure p_f: a – spherical initial particle with volume V_{sp}; b – initial particle approximated by a cylinder with the same volume $V_i = V_{sp}$; c – deformed particle with volume $V_f = V_i = V_{sp}$

microhardness (by 47%) even than that extruded bulk, for which HV is about 1.33–1.35 GPa [3, 4]. Such an increase of the microhardness of coatings as compared to that of specimens extruded can be explained with regard for the characteristic of deformation under features CGDS method, namely by the extremely high strain rate ($\dot{e}$) and the low-temperature process. For example, the deformation of powder particles during the spraying of coatings occurs at temperatures which are by 150 K lower than those under conditions of warm ($T = 623$ K) extrusion [3], by accounting for the operation time head pressure p_f, the strain rate of powder particles in coatings reaches the value ($e_c = e/\tau = 1.15 \times 10^7 - 1.15 \times 10^5$ s^{-1}) which is higher by 4–6 order magnitude than that indicative of the extrusion process.

The modern ideas imply that increasing the strain rate ($\dot{e}$) and especially decreasing the temperature cause the enhancement of the yield stress (σ_γ), although material deformation under the same pressure decreases. It was shown [11] that the yield stress is directly related to the hardness:

$$HM = 1.08HV = c\sigma_\gamma. \qquad (5)$$

Here, HM is the Meyer hardness, HV is the Vickers hardness, and c is the constraint factor which is equal to 3 [3, 11].

It is worth noting that the significant enhancement (by two times) of the yield stress for powdered $Al_{94}Fe_3Cr_3$ and $Al_{94}Fe_{2.5}Cr_{2.5}Ti_1$ alloys after their consolidation in a coating is accompanied by only a small ($\sim$ by 10%) decrease of the plasticity characteristic δ_H down to 0.83 (Table). This value is quite sufficient for the efficient exploitation of surface layers without fracture under loading [12].

Thus, it could be concluded that the CGDS method demonstrates a significant advantage in strengthening the material under low temperatures, allowing one to obtain both the coating and adjacent regions of a steel substrate, for which mechanical properties are determined not only by the phase transformation but also by the hardening due to SPD.

5. Conclusions

1. By employing the $Al_{94}Fe_3Cr_3$ and $Al_{94}Fe_{2.5}Cr_{2.5}Ti_1$ alloys, the efficiency of applications of cold gas-dynamic spraying technique as for the conservation of disperse particles (in particular, particles with sizes < 100–200 nm) of the metastable quasicrystalline phase is experimentally substantiated. Under a processing of quasicrystals, no alterations of the shape and size of quasicrystalline particles occur, while a plastic deformation of powder particles to the elliptic shape with the aspect ratio $k_f = 4.7$ results in the formation of dense coatings with a porosity of at most 3% without structural defects like cracks and delaminations.

2. It is shown that, unlike other methods of gas thermal spraying (in particular to plasma and detonation spraying) applications of the CGDS technique is much effective for hardening the coatings and substrate under low temperatures, allowing one to control their mechanical properties not only by a variation of the phase composition but also by hardening

due to SPD with extremely high strain rates ranging from $e_c = 1.15 \times 10^7$ to 1.15×10^5 s^{-1}.

3. It is found that the microhardness of coatings in the $A1_{94}Fe_3Cr_3$ system attains $HV = 1.95$ GPa, by exceeding twice the microhardness of the initial powders. Microhardness of coating increases additionally to $HV = 1.99$ GPa in the $Al_{94}Fe_{2.5}Cr_{2.5}Ti_1$ system due to the doping with Ti. Microhardness of a steel substrate within the transient zone adjacent to interface increases by 50%, resulting in the value indicative of the coating,

4. It is shown that the significant increase in the microhardness of $Al_{94}Fe_3Cr_3$ and $Al_{94}Fe_{2.5}Cr_{2.5}Ti_1$ coatings is accompanied by a small ($\sim$ by 10%) decrease of the plasticity characteristic δ_H from a value of 0.91–0.92, which is inherent to materials with plastic behavior under conditions of tension and bending, to 0.83. Nevertheless, this is sufficient for the efficient exploitation of surface layers without fracture under loading.

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ПОКРИТТЯ ХОЛОДНОГО ГАЗОДИНАМІЧНОГО НАПИЛЕННЯ НА ОСНОВІ СПЛАВУ Al–Fe–Cr З НАНОРОЗМІРНИМИ КВАЗІКРИСТАЛІЧНИМИ ЧАСТИНКАМИ

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Р е з ю м е

На прикладі порошкових жароміцних алюмінієвих сплавів $Al_{94}Fe_3Cr_3$ та $Al_{94}Fe_{2,5}Cr_{2,5}Ti_1$, отриманих методом водяного розпилення, у роботі експериментально обґрунтовано ефективність способу холодного газодинамічного напилення щодо консолідації металевих частинок шляхом інтенсивної пластичної деформації із збереженням в їх структурі дисперсних частинок метастабільної квазікристалічної фази з нано- та субмікронними розмірами (< 100–200 нм). Розвинуто модель пластичного деформування порошкових частинок металевого сплаву в умовах холодного газодинамічного напилення та досліджено його вплив на структуру й механічні властивості отриманих покриттів та підкладки.