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Obtaining functional gradient coatings based on Al_2O_3 by detonation spraying

The article deals with the phase composition and hardness of Al_2O_3 coatings obtained by detonation spraying. It was found that a decrease in the delay time between shots is leading to an increase in the hardness and elastic module of Al_2O_3 coatings. It was found based on X-ray diffraction analysis that the main reason for the increase in hardness with a decreasing in the delay time between shots is associated with increases in the volume fraction of α- Al_2O_3 phase. A high content of the more ductile γ-Al_2O_3 phase at the substrate-coating interface leads to an increase in adhesion characteristics, and a high content of the α-Al_2O_3 phase on the coating surface provides high hardness and wear resistance. The studies of X-ray diffraction presented that the highest phase content is achieved when the coatings are formed with a delay time between shots of 0.25 s. It was found that increase in the volume fraction of the α-Al_2O_3 phase is caused by the secondary recrystallization γ → α, which occurs due to the heating of particles during coating formation, i.e. due to increase in temperature above 1100 ºC in single spots of the coating when they are put each other.

Keywords: detonation spraying, gradient coating, aluminum oxide, structure, hardness, wear resistance, phase, temperature.

Introduction

Currently, methods of applying powder coatings are the effective remedy of increasing the reliability and durability of structural materials for machine parts, equipment, technological and tooling [1]. The restoration and enhancing of machine parts using powder coatings has given rise to a whole family of so-called gas thermal technological processes [2]. The current trend of increasing the adhesion properties of gas thermal coatings is directed to improving the speed of sprayed particles. Therefore, there is much interested in high-speed technologies for coating deposition, which are characterised by high performance, universality, simplicitў of automation, and almost unlimited sizes of the surfaces to be coated. Geothermal high-speed methods for obtaining coatings include methods of detonation, high-velocity air-oxygen fuel (HVAOF) and high-velocity oxygen fuel (HVOF) spraying [3–5]. Among them, prospective is detonation spraying [6–9]. However, widely used the detonation method for strengthening components and equipment parts for the oil and gas industry, shipbuilding, metallurgy, gas turbine engineering, etc. requires a significant increase in the properties of the obtained coatings. It is related to the components and parts of the above equipment operate under the simultaneous influence of various environments and loads, the values of which in many cases exceed the maximum permissible values for existing detonation coatings. Significantly increase the properties of detonation coatings can be achieved by spraying various materials (powders) in several layers, which allows you to obtain coatings with special characteristics. This is also possible when using gradient coatings of the same material, which structure and properties change in the depth of the coatings. Such coatings have the necessary specified properties of the outer layers that are exposed to the direct impacts on the external environment. Besides, compared to a multi-layer coating, they reduce the difference between the physical and mechanical characteristics of the coating and the base. Therefore, the stress jump occurs when loading at the border of the interface layers is reduced.

In connection with, the task was in this work to obtain and study functional gradient coatings based on aluminium oxide obtained on a single-barrel detonation unit by changing the technological parameters during spraying with the use of only one dispenser, i.e. one type of powder.

Methods and materials

Stainless steel 12Kh18N10T was chosen as the substrate. Before coating, the samples were exposed to sandblasting. For the obtain coatings of zirconium oxide was used powders of corundum (α-Al_2O_3). Powder particle size is 22–45 mμ. Detonation coatings were obtained by a new generation of CCDS2000 (Computer Controlled Detonation Spraying) computerized detonation spraying system [10]. Table 1 shows the modes for obtaining functional gradient coatings based on Al_2O_3.

Table 1

Technological parameters for obtaining functional gradient coatings Al_2O_3

Ratio of O_2/C_2H_2	Filling volume of the barrel, %	Spray distance, mm	Number of shots fired	Delay time between shots, s
1.856	63	250	20	1.00–0.25

The general view and schematic diagram of the detonation spraying process are shown in Figure 1. The channel inside the gun barrel is filled with gases using a high-precision gas distribution system, which is controlled by a computer. The process begins with filling the channel with a carrier gas. After that, a particular portion of the explosive mixture is fed in such a way that a layered gas medium is formed, consisting of an explosive charge and a carrier gas. Using a carrier gas stream for the powder is injected into the barrel (using a computer-controlled feeder) and forms a cloud. The substrate is allocated at a certain distance from the output from the barrel. After some of the gunpowder is injected, the computer sends a signal to initiate detonation. is is realized by an electric spark. The duration of the explosive charge combustions is about 1 ms. In the explosive mixture, a detonation wave is formed, which in the carrier gas passes into a shockwave. The detonation products (heated to 3500–4500 K) and the carrier gas (heated by the shockwave to 1000–1500 K) move at supersonic speed. The interaction time of gases with the sprayed particles is 2–5 ms. The particle speed can reach 800 ms^{-1} [11].

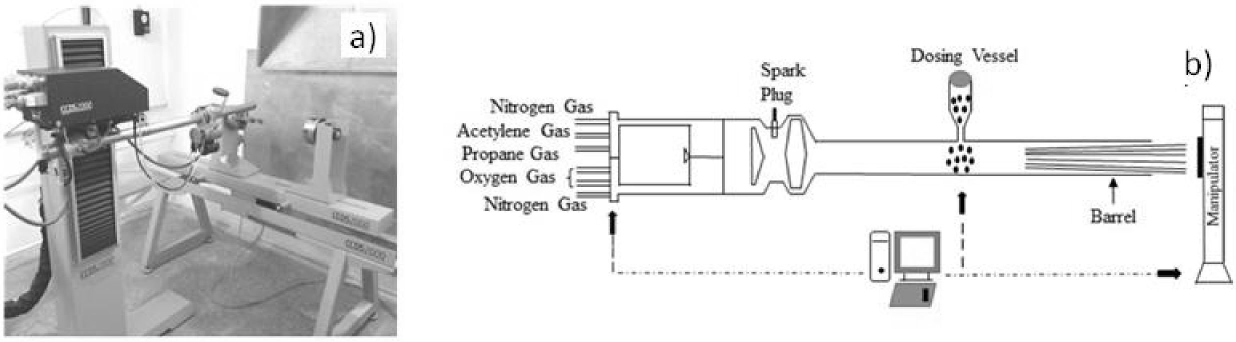


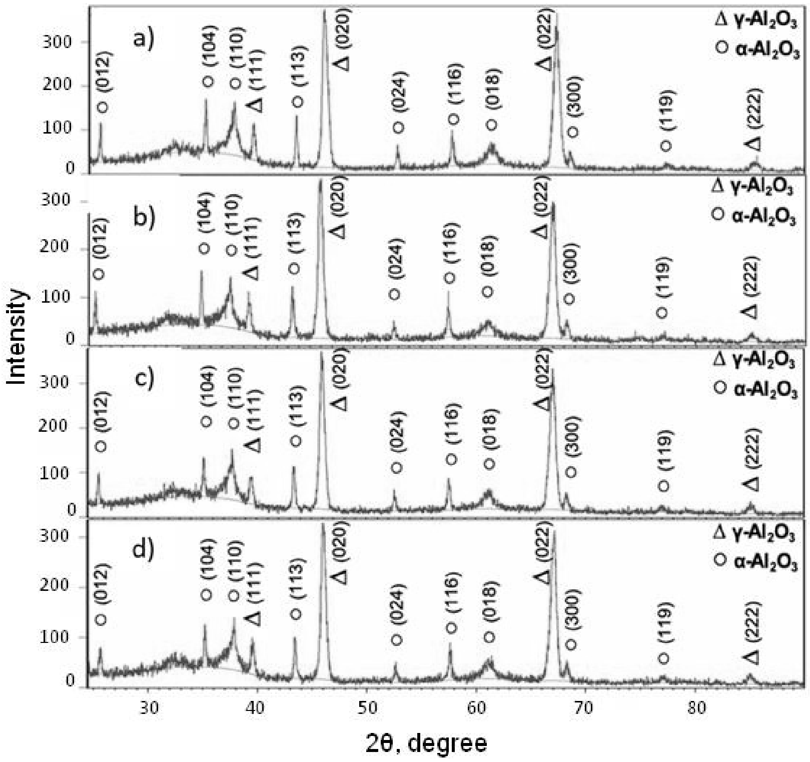
Figure 1. Computerized detonation complex CCDS2000 (*a*) and its schematic diagram (*b*)

The phase composition of the samples was studied by X-ray diffraction analysis on an X'pert Pro diffractometer using CuKα-radiation. The measurement of hardness and modulus of elasticity was determined by indenting on a nano hardness «NanoScan-4D compact» by state standard R 8.748–2011 and ISO 14577. The tests were performed at a load of 100 mN. Tribological tests for sliding friction were performed on a high-temperature tribometer TRB^3 using the standard «ball-disk» method (international standards ASTM G 133–95 and ASTM G 99). As a counterbody was used a 3.0 mm diameter ball made of SiC-coated steel. The tests were performed at a load of 10 N and a linear velocity of 3 cm/s, with a wear radius of 4 mm, and a friction path of 81 m. Tribological characteristics of the modified layer were characterized by wear intensity and friction coefficient. All types of experimental studies were performed at the Scientific Research Center «Surface Engineering and Tribology» of the Non-limited profit company Sarsen Amanzholov East Kazakhstan University.

Results and discussion

In work [12], was studied the effect of the detonation spraying mode on the structure and properties of Al_2O_3 coatings. Determined, a decrease in the delay time between shots brings to an increase in the hardness and elastic modulus of Al_2O_3 coatings. Based on X-ray phase analysis was found, the main reason for the increase in hardness with a decrease in the delay time between shots is associated with an increase in the volume fraction of the α-Al_2O_3 phase. X-ray phase analysis showed the highest content of the α-phase is achieved when coatings are formed with a delay between shots of the order of 0.25 s. It was found, the increase in the volume fraction of the α-Al_2O_3 phase is caused by secondary recrystallization of γ → α, which occurs due to the warming of the particles during the coating formation, i.e., due to an increase in the temperature above 1100 ºC in individual coating spots when they overlap each other. In this regard, we studied the possibility of obtaining functional gradient coatings, which the gradient of structure and properties is based on a gradual increase in the volume fraction of the α-Al_2O_3 phase from the substrate to the outer layer.

Figure 2 shows the diffractograms of a multilayer gradient coating obtained by a gradual decrease in the delay time between shots during spraying. Multilayer coating consists of four layers. All coating layers are contained the γ-Al_2O_3 and α-Al_2O_3 phases.



a — fourth layer; *b* — third layer; *c* — second layer; *d* — first layer

Figure 2. Diffractogram of the coating

Herewith, there is a gradual increase in the intensity of the α-Al_2O_3 phase reflexes from the substrate to the surface. The results of the quantitative analysis showed that the volume fraction of the α-Al_2O_3 phase from the substrate to the outer layer gradually increases. The volume fraction of the α-Al_2O_3 phase in the first layer is 24 %, in the second layer 30 %, in the third layer 31 %, in the fourth layer, i.e. on the coating surface the volume fraction of the α-Al_2O_3 phase is 34 %.

Figure 3 shows a graph of the microhardness distribution over the thickness of gradient coatings. The graph of the dependence of microhardness on the depth of the gradient coating Al_2O_3 shows an unequal distribution of microhardness: the coating near the transition layer has a lower microhardness value, indifference the upper part of the coating. Herewith, there is a uniform increase in microhardness from the substrate to the surface of the coating.

A layer-by-layer analysis was performed of the functional gradient coating of Al_2O_3. After spraying each layer, was studied the structure and tribological characteristics of the coatings. Table 2 shows data of layers of functional gradient coating Al_2O_3 the structure and tribological characteristics. Experimental data clearly illustrates the correlation between the structural and tribological characteristics of layers of Al_2O_3 functionally gradient coating.

The generalized data given in the Table 2, the dependence of the wear intensity, hardness, and friction coefficient of the Al_2O_3 coating layers on its structural and phase states is clearly traced. The wear resistance of the first, second and third layers (delay time between shots 1 s) is significantly lower than that of the fourth layer (delay time between shots 0.25 s). The fourth layer, consisting of γ-Al_2O_3 (66 %) and α-Al_2O_3

(34 %), showed high tribological characteristics. The effects of increasing hardness and wear resistance are directly related to the volume fraction of the α-Al_2O_3 phase, which are formed during the spraying process due to heating of the coating surface.

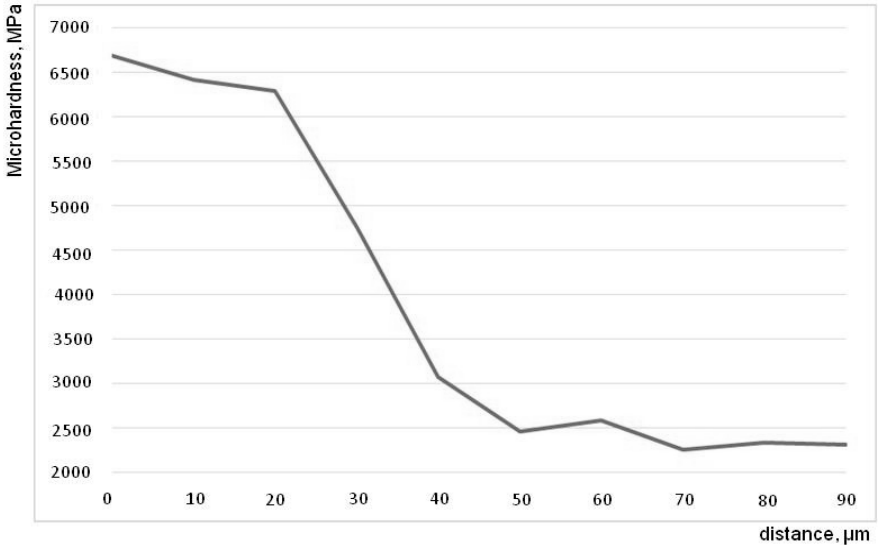


Figure 3. Graph of hardness distribution by depth of gradient coatings Al_2O_3

Table 2

Experimental data on the structure and tribological characteristics of functional gradient coating layers Al_2O_3

Coating layer	Phase composition	Nanohardness, GPa	Young modulus, GPa	Coefficient of friction	Wear intensity, $mm^3/(m{\cdot}N)$
First layer	γ-Al_2O_3 (76 %) and α-Al_2O_3 (24 %)	10.87	207.70	0.42	$3.83{\cdot}10–^5$
Second layer	γ-Al_2O_3 (70 %) and α-Al_2O_3 (30 %)	11.03	159.97	0.48	$4.16{\cdot}10–^5$
Third layer	γ-Al_2O_3 (69 %) and α-Al_2O_3 (31 %)	11.72	206.48	0.41	$3{,}73{\cdot}10–^5$
Fourth layer	γ-Al_2O_3 (66 %) and α-Al_2O_3 (34 %)	16.33	270.64	0.37	$1{,}60{\cdot}10–^5$

Conclusion

A method for obtaining multilayer gradient coatings based on Al_2O_3 with various modifications, varying the technological modes of detonation spraying has been developed. The developed method allows obtaining gradient coating structures on a single barrel detonation installation with a unique dispenser by changing the delay time between shots. It is determined that a decrease in the delay time between shots leads to an increase in the hardness, modulus of elasticity and wear resistance of Al_2O_3 coatings. Based on X-ray phase analysis, it was found that the main reason for the increase in hardness with a decrease in the delay time between shots is associated with an increase in the volume fraction of the α-Al_2O_3 phase. A high content of the more plastic γ-Al_2O_3 phase at the substrate-coating border leads to an increase in the adhesion characteristics, and a high content of the α-Al_2O_3 phase on the coating surface provides high hardness and wear resistance. Therefore, we obtained a functional gradient coating in which the gradient of structure and properties is based on a gradual increase in the volume fraction of the α-Al_2O_3 phase from the substrate to the outer layer.

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Детонациялық тозаңдату әдісімен Al_2O_3 негізінде функционалдық-градиенттік жабындарды алу

Мақалада детонациялық бүрку режимінің Al_2O_3 жабындарының құрылымы мен қасиеттеріне әсері зерттелді. Ату арасындағы кідіріс уақытының азаюы Al_2O_3 жабындарының қаттылығы мен серпімділік модулінің жоғарылауына әкелетіні анықталды. Рентгендік фазалық талдау негізінде кадрлар арасындағы кідіріс уақытының азаюымен қаттылықтың жоғарылауының негізгі себебі α-Al_2O_3 фазасының көлемдік үлесінің артуымен байланысты екендігі анықталды. Төсем мен жабын шекарасындағы пластикалық γ-Al_2O_3 фазасының негұрлым көп мөлшері адгезиялық сипаттамаларының жоғарылауына әкеледі, ал жабындар бетіндегі α-Al_2O_3 фазасының көп мөлшері жоғары қаттылық пен тозуғатөзімділікті қамтамасыз етеді. Рентгендік фазалық зерттеу көрсеткендей, α фазасының ең көп мөлшері 0,25 с бүрку арасындағы кідіріспен жабындарды қалыптастыру кезінде қол жеткізіледі. Фазаның α-Al_2O_3 көлемдік үлесінің артуы γ → α-ның қайталамалы қайта кристалдануымен байланысты екендігі анықталды, бұл жабынды қалыптастыру кезінде бөлшектердің қызуы нәтижесінде пайда болады, яғни олар бір-біріне қабаттасқан кезде жабынның бір дақтарында температураның 1100 ºС-тан жоғары көтерілуіне байланысты.

Кілт сөздер: детонациялық бүрку, градиентті жабын, алюминий оксиді, құрылым, қаттылық, тозуғатөзімділік, фаза, температура.

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Получение функционально-градиентных покрытий на основе Al_2O_3 методом детонационного напыления

В статье было изучено влияние режима детонационного напыления на структуру и свойства покрытий Al_2O_3. Определено, что уменьшение времени задержки между выстрелами приводит к повышению твердости и модуля упругости покрытий Al_2O_3. На основе рентгенофазового анализа установлено, что основная причина повышения твёрдости при уменьшении времени задержки между выстрелами связана с повышением объемной доли α-Al_2O_3 фазы. Большое содержание более пластичной γ-Al_2O_3-фазы на границе подложка–покрытие приводит к увеличению адгезионных характеристик, а большое содержание α-Al_2O_3-фазы на поверхности покрытий обеспечивает высокую твердость и износостойкость. Рентгенофазовое исследование показало, что наибольшее содержание α-фазы достигается при формировании покрытий с задержкой между выстрелами порядка 0,25 с. Установлено, что увеличение объемной доли α-Al_2O_3 фазы обусловливается вторичной перекристаллизацией γ → α, происходящей вследствие отогрева частиц при формировании покрытия, т.е. при возрастании температуры выше 1100 ºC в единичных пятнах покрытия в результате их наложения друг на друга.

Ключевые слова: детонационное напыление, градиентное покрытие, оксид алюминия, структура, твердость, износостойкость, фаза, температура.

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