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Comparative study of the structure and properties of homogeneous and gradient Ni-Cr-Al coatings

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This paper compares the structure and properties of homogeneous and gradient coatings in the Ni-Cr-Al system obtained by detonation spraying. According to X-ray analysis, only the $CrNi_3$ phase appears in the homogeneous coating, and $CrNi_3$, Al, and NiAl phases appear on the gradient coating. The elements distribution graphs show that a small amount of aluminum is distributed over the depth of the homogeneous coating and in the gradient coating. The distribution of aluminum in the gradient Ni-Cr-Al coating gradually increases from the depth to the surface, and a high amount of aluminum forms in the coating surface. According to EDS analysis, a small amount of aluminium is distributed on the surface of the homogeneous coating and a large amount on the gradient coating. In the gradient coating, aluminium gradually increases from the substrate surface to the coating surface. Also, the gradient coating has a higher hardness than the homogeneous coating.

Keywords: gradient coating; Ni-Cr-Al coating; phase; structure; detonation spraying; microhardness; EDS analyses

Introduction

Protective coatings are used to protect industrial technologies from wear and corrosion [1-4]. Ni-Cr-Al based protective coatings are often used to preserve hightemperature parts of thermal power plants from oxidation and heat corrosion [5-8]. The first use of this coating for this purpose was proposed in the 1970s [9]. The main advantage of this system is that nickel and chromium give strength, and aluminium, in contact with oxygen at high temperatures, prevents oxidation of the surface, forming a protective film of Al_2O_3 [10-13]. However, the amount of aluminium on the surface varies in the range 10-14 per cent. Therefore since 1975, more attention has been paid to studying the uniform distribution of aluminium on the surface [14]. Various modes and methods have been proposed for this purpose. One of the methods developed in recent years is to obtain a gradient structure coating.

The structure and, consequently, the properties of gradient coatings vary depending on their thickness. Gradient coatings exhibit lower stresses at the substratecoating interface and can be designed for operating conditions. A distinctive feature of the general gradient coating that distinguishes it from other coatings is the continuous distribution of coating elements on the surface [15-18].

Ni-Cr-Al coatings have been obtained by various methods [19-21]. One of them is the method of detonation spraying [22-24]. Detonation spraying technology is an effective method that produces a coating with very low porosity and high adhesion. This provides solid, wear-resistant and dense microstructural coatings and is the best method of thermal spraying. The detonation spraying process can be carried out at temperatures up to 4000° C in a combustion chamber with shock wave velocities reaching 3500 m/s.

Various methods are used to obtain gradient coatings by detonation spraying. One way is to apply gradient coatings by alternating shots from two dispensers with different powders [25]. However, the coating obtained by this method has a layered structure, which does not give gradient coatings with unique characteristics. It is also possible to obtain gradient coatings using a single dispenser by replacing powders with different concentrations of a particular element after a certain number of shots. This method is time-consuming, and when replacing powders on the dispenser, the applied layer is oxidized and cooled to room temperature, which leads to a deterioration in the cohesive strength of the coating. Considering the disadvantages of the available methods of applying gradient coatings by detonation spraying, we have developed a new method for obtaining gradient coatings. We use a single dispenser detonation unit and change the technological modes during the spraying process in an automated way. We based our approach on our previous works [24, 26] in which we found that the phase and elemental composition of coatings depend on the gas mixture barrel filling degree. The present paper gives the results of a comparative study of the structure and properties of homogeneous and gradient Ni-Cr-Al coatings obtain using our detonation spraying method.

Experimental methods

Ferrite-pearlite steel 12Kh1MF was chosen as the substrate. The chemical composition of 12Kh1MF steel is shown in Table 1. The samples were grinded using

MIRKA grinding paper up to 1200 to achieve a uniform and flat surface. After grinding, sandblasting of the samples was carried out. To obtain coatings based on Ni-Cr-Al, mixtures of Ni Cr (Ni20Cr80) and Al (99.99%) powders were used in the following proportions (in mass fractions): 80%NiCr (Ni20Cr80) and 20% - Al (99.99%). The size of the powder particles is 30-45 microns. Preliminary mechanical activation of the powder mixture was carried out in a planetary ball mill PULVERISETTE 23. The mechanical activation time was 0.5 hours with a frequency of 30 Hz.

Table 1.
Chemical composition of steel 12Kh1MF.

C	Si	Mn	Ni	S	P	Cr	Mo	V	Cu
0.1-0.15	0.17 - 0.37	0.4-0.7	≤0.3	≤0.025	≤0.03	0.9-1.2	0.25-0.35	0.15-0.3	≤0.2

To obtain coatings, the CCDS2000 detonation complex (LIH SB RAS, Novosibirsk, Russia) was used, which has a system of electromagnetic gas valves that regulate the supply of fuel and oxygen and control the system's purging. The detail of this system is described in [27]. The general view and schematic diagram of the detonation spraying process are shown in Figure 1. The gun barrel is filled with gases using a highprecision gas distribution system controlled by a computer. The process begins with filling the barrel with carrier gas as a carrier gas was used nitrogen.

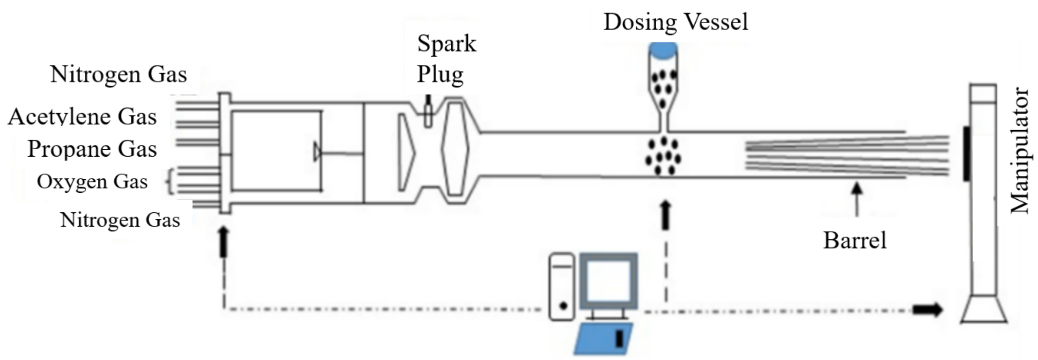

Figure 1. Computerized detonation complex CCDS2000: general view (a) and schematic diagram of the installation (b).

Homogeneous Ni-Cr-Al coating was obtained 50% barrel filling volume. Gradient coating of Ni Cr-Al was obtained by the developed method described in work [24]. This method obtains coatings by gradually changing the barrel filling volume with explosive gas mixture during detonation deposition. Gradient coating was obtained by gradually reducing the barrel filling volume from 50% to 25%. Table 2 shows the modes of getting homogeneous and gradient coatings based on Ni-Cr-Al.

Table 2.
The modes of obtaining homogeneous and gradient coatings based on Ni-Cr-Al.

Name	Ratio O_2/C_2H_2	Barrel filling volume, %	Spraying distance, mm	Shot number
Homogeneous Ni-Cr-Al coating	1.856	50%	250	20
Gradient Ni-Cr-Al coating	1.856	50%	250	5
		40%		5
		30%		5
		25%		5

X-ray phase studies of samples were performed by X-ray diffraction analysis on an X'PertPRO diffractometer (Philips Corporation, Nederland). Diffractograms were taken using CuKa radiation (λ =2.2897 A°) at a voltage of 40 kV and a current of 30 mA. The decoding of diffractograms was carried out using the HighScore program. The microhardness from the coating's surface was measured using the Metolab-502 testing machine (Metolab, Russia) according to GOST 9450-76. The morphology of the crosssection of the samples was studied by scanning electron microscopy (SEM) using backscattered electrons (BSE) on a scanning electron microscope JSM-6390LV (Jeol, Tokyo, Japan) at accelerated voltages.

Result and discussion

Previously, we published [21-24] works on studying the effect of the barrel filling volume with gases on the structure and tribological properties of coatings based on Ni-Cr-Al. It was found that by varying the barrel filling volume during spraying, gradient coatings based on Ni-Cr-Al can be obtained [24]. Further, we will show comparative results of structure and properties of homogeneous and gradient Ni-Cr-Al coatings.

Figure 2 shows diffractograms of single-layer and gradient nickel coatings. The Figure shows that the single-layer coating consists of $CrNi_3$. Due to the low aluminium content ($\approx$ 20%), no Al peaks are observed in the diffraction pattern of the single-layer coating.

The gradient coating consists of phases $CrNi_3$, Al and Ni. The formation of Al and NiAl phases is associated with an increase in aluminium concentration in the surface layer of coatings.

Figure 3 shows graphs of the elements distribution by coating depth obtained by optical emission spectrometry. From the graph, it can be seen that a small amount of aluminum element is distributed over the depth of the homogeneous coating, and in the gradient coating, distribution aluminum gradually increased from the coating depth to the surface coating, and a high amount of aluminum is formation coating surface. At the same time, in a homogeneous coating, nickel

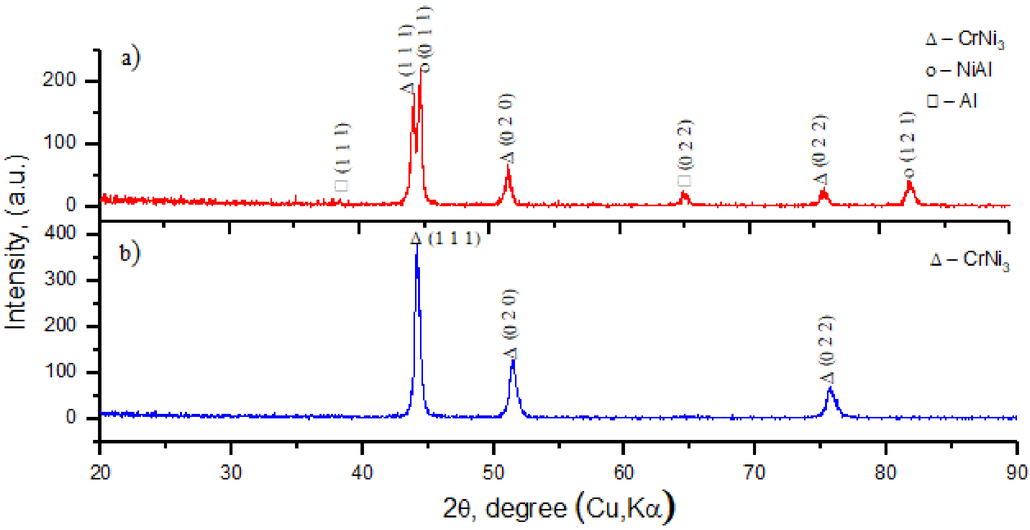

Figure 2. Diffractograms of single-layer and gradient coatings Ni-Cr-Al.

and chromium elements by depth of the coating are distributed uniformly, while in a gradient coating, nickel and chromium elements are distributed mainly on the sample surface, nearing the coating surface they are reduced.

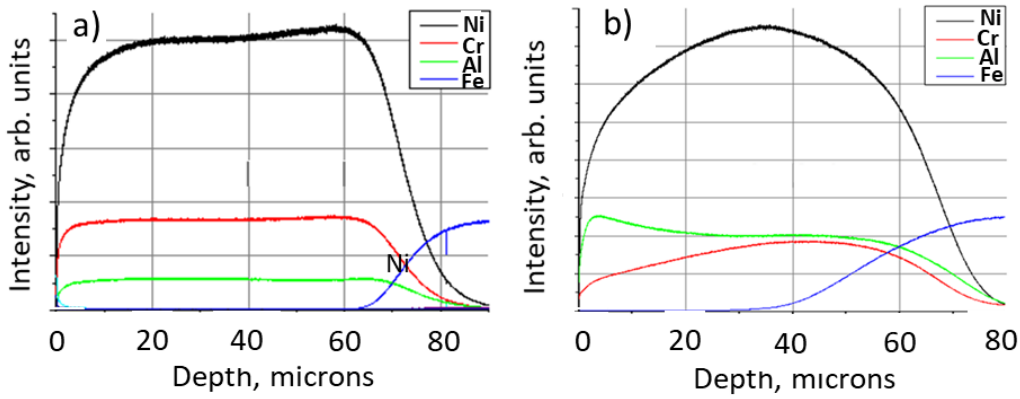

Figure 3. Depth distribution of elements of homogeneous (a) and gradient coatings (b) based on Ni-Cr-Al.

Figure 4a shows SEM image results of the cross-section of the single-layer Ni-Cr-Al coating taken on the sample surface. It can be seen that the microstructure of the coating is uniform compared to the gradient coating (Figure 4b), and aluminium granules quantity insignificantly. The microstructures of transverse cross-sections of samples with gradient coatings show an uneven, highly developed relief layer. Also, the amount of Aliumium granules gradually increases from the surface of the sample to the surface of the coating.

With the help of EDS analysis, the elemental composition of homogeneous and gradient coatings Ni-Cr-Al is determined. The results of the EDS analysis are shown in Table 3 and Table 4. According to the results, it can be seen that a small amount of aluminium is distributed on the surface of a homogeneous coating and a large amount on a gradient coating. At the same time, in the gradient coating, aluminium gradually increases from the sample surface to the coating surface, i.e. it is distributed in a gradient way. The energy dispersion analysis of the coatings showed a content of up to 20% (by weight) oxygen, which is associated with the oxidation of the coatings during the detonation coating since the treatment was carried out in the air.

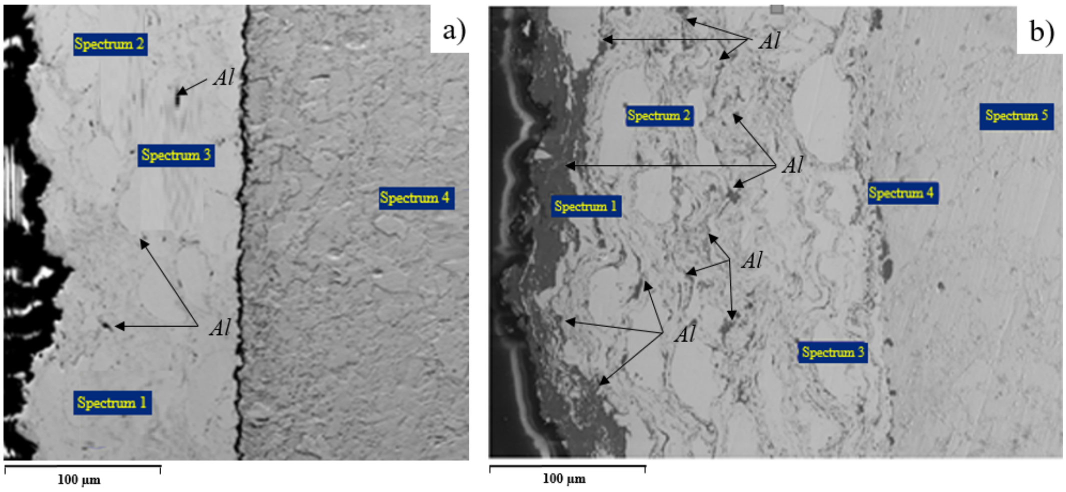

Figure 4. SEM-cross-sectional image of homogeneous (a) and gradient coating (b) based on Ni-Cr-Al.

Table 3.
The elemental composition of homogeneous Ni-Cr-Al coating by EDS analysis.

Spectrum	O	Al	Si	Cr	Mn	Fe	Ni
Spectrum1	3.44	2.36		20.3			73.90
Spectrum2	2.65	1.28		21.59			74.48
Spectrum3	3.55	1.1		20.21			75.14
Spectrum4			0.59	1.23	0.75	94.07	3.36

Table 4.
The elemental composition of gradient Ni-Cr-Al coating by EDS analysis.

Spectrum	O	Al	Si	Cr	Mn	Fe	Ni
Spectrum1	5.74	74.32		6.24			13.7
Spectrum2	6.23	40.98		18.25			34.54
Spectrum3	13.3	25.24		19.64			41.82
Spectrum4		1.43	1.11	8.32	1.09	59.69	28.36
Spectrum5			0.66	2.42	0.73	90.73	5.46

The results of microhardness of homogeneous and gradient Ni-Cr-Al coatings are shown in Figure 5. The effects of increasing hardness are associated with the formation of a gradient structure, in which the surface layer of the coatings contains NiAl phases. NiAl intermetallic compound has several features: low porosity, relatively high melting point, excellent corrosion and oxidation resistance, high strength at elevated temperatures, and relatively low cost. For these reasons, NiAl-based intermetallic is a good candidate for various applications, such as manufacturing blades and other turbine components.

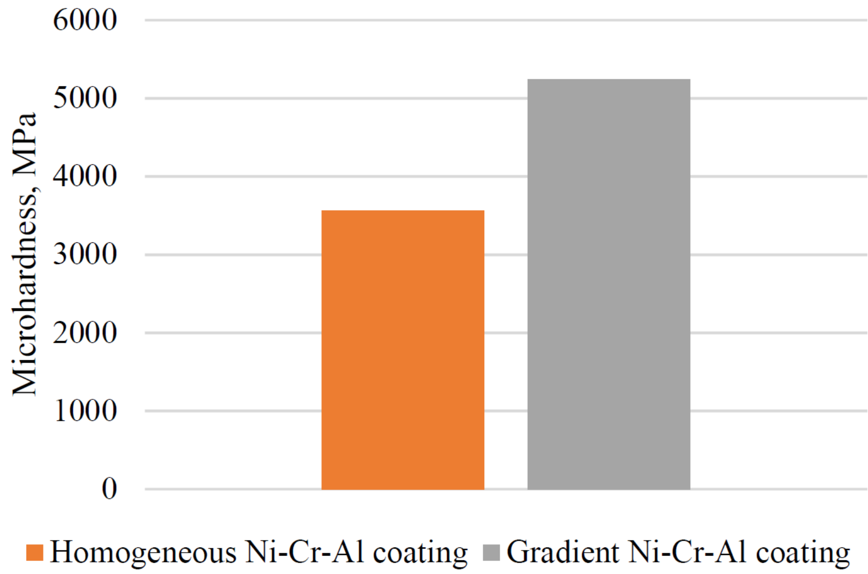

Figure 5. The results of microhardness of homogeneous and gradient Ni-Cr-Al coatings.

Conclusion

In the paper, the results of the structure and properties of homogeneous and gradient coatings were compared. Based on this comparison, we concluded the following conclusion:

- According to the results of X-ray analysis, only the $CrNi_3$ phase appeared from the homogeneous coating when the $CrNi_3$, Al, and NiAl phases were formed on the gradient coating.

- From the graphs of the distribution of the elements, a small amount of aluminum element is distributed over the depth of the homogeneous coating, and in the gradient coating, distribution aluminum gradually increased from the coating depth to the surface coating, and a high amount of aluminum is formation coating surface.

- The SEM image shows the gradient distribution of aluminium over the coating, and a significant amount of aluminium is formed on the coating surface. And in a homogeneous coating, aluminium granules are of low quantity, even granules of aluminium barely noticeable.

- According to the EDS results, a small amount of aluminium is distributed on the surface of a homogeneous coating and a large amount on a gradient coating. At the same time, in the gradient coating, aluminium gradually increases from the sample surface to the coating surface.

- Analysis of the experimental results obtained indicates that the gradient coating has a high hardness than homogeneous coating. The effects of increasing hardness are associated with the formation of a gradient structure, in which the surface layer of the coatings contains NiAl phases.

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References

[1] P.S. Sidky et al., British Corrosion Journal **34**(3) (1990) 171-183. [*CrossRef*]
[2] D. Romanov et al., Journal of Materials Research and Technology **8**(6) (2019) 5515-5523. [*CrossRef*]
[3] B. Swain, Surface Topography: Metrology and Properties **9**(2) (2021) 025039. [*CrossRef*]
[4] Z. Wang, Journal of Alloys and Compounds **828** (2020) 154412. [*CrossRef*]
[5] A. Mokhtar et al., Metals **10**(1) (2020) 42. [*CrossRef*]
[6] G.H. Meng et al., Surface and Coatings Technology **368** (2019) 192-201. [*CrossRef*]
[7] I. Gurrappa, Surface and Coatings Technology **139**(2) (2001) 272-283. [*CrossRef*]
[8] W. Sloof et al., International Journal of Materials Research **100**(10) (2009) 1318-1330. [*CrossRef*]
[9] M.R. Jackson et al., Thin Solid Films **45**(2) (1977) 376. [*CrossRef*]
[10] R. Darolia, International Material Reviews **58**(6) (2013) 315-348. [*CrossRef*]
[11] A. Meghwal et al., Journal of Thermal Spray Technology **29**(5) (2020) 857-893. [*CrossRef*]
[12] K. Ogawa, Turbines-Materials, Modeling and Performance (2015). [*CrossRef*]
[13] R. Lowrie et al., Thin Solid Films **45**(3) (1977) 491-498. [*CrossRef*]
[14] G. Bolelli et al., Surface and Coatings Technology **206**(8) (2012) 2585-2601. [*CrossRef*]
[15] M. Naebe et al., Applied Materials Today **5** (2016) 223-245. [*CrossRef*]
[16] W.Y. Lee et al., Journal of the American Ceramic Society **79**(12) (1996) 3003-3012. [*CrossRef*]
[17] D. Toma et al., Oxidation of Metals **53**(1) (2000) 125-137. [*CrossRef*]
[18] G. Mauer et al., Journal of Thermal Spray Technology **23**(1) (2014) 140-146. [*CrossRef*]
[19] J.C. Pereira et al., Surface Coatings and Technology **338** (2018) 22-31. [*CrossRef*]
[20] C.K. Abdullah et al., Vacuum **180** (2020) 109609. [*CrossRef*]
[21] Jun-guo GAO et al., Transactions Nonferrous Metals Society of China **25** (2015) 817-823. [*CrossRef*]
[22] M. Maulet et al., Eurasian Journal of Physics and Functional Materials **4**(3) (2020) 249-254. [*CrossRef*]
[23] M. Maulet et al., 2020 IEEE 10th International Conference Nanomaterials: Applications & Properties (NAP) (2020) 01TFC17-1-01TFC17-3. [*CrossRef*]
[24] B. Rakhadilov et al., Coatings **11**(2) (2021) 218. [*CrossRef*]

[25] J.H. Kim et al., Surface and Coatings Technology **168** (2003) 275-280. [*CrossRef*]
[26] B.K. Rakhadilov et al., Eurasian Journal of Physics and Functional Materials **4**(2) (2020) 160-166. [*CrossRef*]
[27] V.Y. Ulianitsky et al., Metals **9** (2019) 1244. [*CrossRef*]