https://doi.org/10.46813/2021-131-106

ESTIMATION OF LOCAL INHOMOGENEITY OF MULTILAYER NANOSTRUCTURED ZrN/ZrO_2 COATING

T.S. Skoblo, S.P. Romaniuk, Ye.L. Belkin, T.V. Maltsev

Kharkiv Petro Vasylenko National Technical University of Agriculture, Kharkiv, Ukraine

E-mail: romaniuk.khntusg@gmail.com

Multilayer nanostructured ZrN/ZrO_2 coatings were applied to increase the operational resistance of various machinery parts by using vacuum-arc deposition in Bulat-type facility. To describe the structure formation, a new approach based on optical-mathematical method for processing metallographic images is proposed. The structure formation of the multilayer coating with an assessment of the degree of its inhomogeneity and diffusion processes between the layers is studied. For a reliable assessment, the changes in the horizontal and vertical directions of the images with the choice of optimal intervals were comparatively analyzed. It has been found that the most stable results are achieved using 20 and 25 dots (pixels).

PACS: 52.77.-j; 81.20.-n

INTRODUCTION

In recent years, various wear-resistant coatings have been used for hardening technologies in mechanical engineering, which, due to the effective choice of the components composition, can provide various consumer properties increasing tool-life. It was shown in [1-5] that the effectiveness of hardened nanostructured coatings with single or multilayer architecture provided an increase in the operational resistance of tools by 7-15 times. At the same time, in such coatings, degradation processes and composition deviations were studied less intensively. The aim of the researchwas to study the structural inhomogeneity during formation of multilayer ZrN/ZrO_2 coating with an assessment of the degree of diffusion processes between layers using complex optical-mathematical approaches.

EXPERIMENTAL SETUP

To implement the technological process of hardening products, a multilayer coating was applied to cast steel (packing knives used in the confectionery industry D3 ASTM A681) by the ion-plasma deposition method with partial separation of the micro-droplet component of the plasma flow in Bulat-6 facility. To increase the adhesion strength of the coating, thin Zr layer with a thickness of 50 nm was preliminarily applied to the substrate.

To assess the quality of the coating, electron microscopy with images at various magnifications (up to 10.000 times), local X-ray spectral analysis, and optical-mathematical description of structure formation with an assessment of the degree of inhomogeneity of different zones of the layers were used.

When using the previously developed optical-mathematical analysis [6, 7] a new program was specially developed to analyze the variability of structure formation on metallographic images by indicators of inhomogeneity. It was assessed by dependencies (1) and (2). They included positive and negative degrees in the horizontal and vertical directions at 19 image intervals and 12 uniformly distributed horizontal zones of the multilayer coating along its cross section.

$$H_1 = \frac{n\prod_{i=1}^{n} c_i}{\sum c_i^n}, \quad (1)$$

$$H_2 = \frac{n\prod_{i=1}^{n} c_i^{-1}}{\sum c_i^{-n}}. \quad (2)$$

The degree of heterogeneity of different zones of the ZrN/ZrO_2 multilayer coating and the Zr sublayer was estimated by the optical-mathematical method based on analysis using a different number of points (pixels).

RESULTS AND DISCUSSION

When assessing the formed degree of phase inhomogeneity, intervals that correspond to a different number of points – 2, 6, 10, 15, 20, 25, 30, 35 were proposed. The corresponding calculation was performed using the formula (1), which Table 1 presents. At the same time, the general structure formation in the horizontal and vertical directions of the formed layers in the coating was also analyzed. It was found that the minimum degree of heterogeneity of the formed coating bands corresponds to those close indicators in the assessment of zones by the number of points 15, 20, 25, 30, and 35, i.e. any number chosen to determine this indicator will consistently reflect the achieved state of the structure during coating. At the same time, based on the minimum number of points, we can get an idea of possible local deviations in the degree of heterogeneity of structure formation.

So, when analyzing the minimum number of points 2 and 6 in the horizontal direction, the indicators of the minimum degree of heterogeneity are overestimated and reach, on average, 58.3 and 13.6 %, respectively.

At the same time, the proportion of structures corresponding to the maximum degree of heterogeneity and estimated at such points varies from 0 to 0.033 (on average 0.001 %).

Table1

Average degree of horizontal heterogeneity of the coating

Heterogeneity according to the analysis interval, %																			Number of points
max	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	min	
0	0	0.003	0	0	0	0	0	0.004	0	0.011	0	0.005	0	0.13	0.276	0.997	40.31	58.25	2
0.03	0.01	0.02	0.05	0.05	0.069	0.14	0.27	0.57	1.04	0.94	2.14	5.44	5.54	10.81	19.91	30.42	8.96	13.58	6
0.18	0.19	0.41	1.02	1.64	1.468	2.43	4.99	5.83	4.25	12.87	5.28	15.66	12.23	12.19	7.75	3.92	1.26	6.42	10
1.85	3.46	5.26	6.28	6.70	9.229	10.34	9.40	10.24	9.18	5.29	8.43	3.67	2.14	1.38	1.26	0.64	0.53	4.7	15
10.84	12.96	13.19	11.39	11.65	8.946	8.77	5.18	4.24	2.70	2.16	0.7	1.03	0.48	0.34	0.28	0.26	0.51	4.34	20
30.43	20.59	13.80	10.72	7.42	4.171	3.12	1.63	1.08	0.65	0.50	0.34	0.20	0.14	0.13	0.21	0.34	0.30	4.2	25
54.37	18.76	10.4	4.86	2.77	1.496	0.72	0.66	0.32	0.20	0.16	0.11	0.08	0.09	0.10	0.17	0.34	0.27	4.19	30
73.36	12.6	4.49	2.10	0.98	0.488	0.36	0.19	0.14	0.08	0.06	0.06	0.05	0.11	0.13	0.11	0.33	0.26	4.06	35

The reduced stability of the local structure (increase x6500) is characterized by the assessment of heterogeneity by 10 points. This applies to both minimum and maximum indicators. The observed may be the result of insufficient statistical sampling.

The most stable results are typical when assessing the degree of maximum heterogeneity of the coating structure by 25 points and it is 30.43 % and, to a greater extent, manifests itself due to a decrease in the proportion of the most stable phase – ZrN. At the same time, it was revealed that the use for the analysis the readings by 35 points the maximum heterogeneity of the structure reaches 73.36 % due to the large sampling interval, which does not take into account local variability. It can be assumed that in this case pure zirconium is the stable phase and its fraction does not exceed 4.1 %. The greatest degree of inhomogeneity of the phase distribution can manifest itself only when analyzing by 2.6 and 10 points.

The same tendency is typical for the assessment of structure formation in the vertical direction with respect to the coating layers (Table 2). However, already starting from the assessment by 10 points, there is a noticeable difference in the minimum degree of heterogeneity, and it increases at 35 points up to 16 %, and the maximum decreases to 0.85 % (~ 5 times). The observed decrease in the degree of inhomogeneity in this version of the assessment can be explained by diffusion processes occurring along the boundaries of zones near the transition layers of ZrN/ZrO_2, which are calculated in vertical direction. Therefore, the heterogeneity of structure formation in the vertical direction (in individual assessment zones) is slightly higher than in the horizontal direction.

Table 2

Average degree of vertical heterogeneity of the coating

Heterogeneity according to the analysis interval, %																			Number of points
max	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	min	
0	0	0.004	0	0.001	0.001	0.001	0	0.006	0	0.026	0	0.017	0.003	0.247	0.651	1.607	44.62	52.80	2
0.12	0.04	0.04	0.06	0.08	0.1	0.25	0.45	0.92	1.41	1.59	3.31	6.73	7.22	12.79	21.06	27.62	6.32	9.87	6
0.32	0.40	0.88	1.92	2.94	2.72	4.29	6.55	8.23	5.85	14.04	6.91	14.16	10.35	8.80	4.6	1.72	0.67	4.63	10
6.04	8.08	9.24	9.27	8.9	10.06	10.05	8.15	8.47	6.37	3.48	4.56	1.61	0.8	0.41	0.46	0.23	0.49	3.29	15
29.17	16.72	13.64	10.49	8.62	6.12	4.92	2.68	1.79	1.01	0.71	0.16	0.28	0.16	0.14	0.12	0.12	0.49	2.62	20
56.87	17.95	9.31	5.77	3.39	1.58	1.02	0.43	0.25	0.159	0.15	0.10	0.11	0.09	0.12	0.11	0.18	0.37	2.03	25
79.59	10.52	4.24	1.52	0.69	0.35	0.18	0.18	0.11	0.10	0.09	0.08	0.10	0.07	0.08	0.10	0.18	0.37	1.44	30
91.49	4.38	1.09	0.44	0.25	0.13	0.11	0.08	0.08	0.08	0.07	0.07	0.07	0.08	0.06	0.10	0.19	0.35	0.86	35

The performed studies of structure formation have confirmed the most effective approach to the choice of the points number for the optical-mathematical description and reliable assessment of the coating heterogeneity.

The studies also focused on the transition zone: base metal-coating, where the application of pure zirconium was used as a substrate to ensure good adhesion. Then the first layer of ZrO_2 coating was applied. The analysis found that its homogeneity reaches 48.6 % (the proportion of pure Zr), and the greatest heterogeneity can be formed due to diffusion processes both from the base metal and from the coating. Layer-by-layer micro-X-ray spectral analysis of the inhomogeneity of the components distribution was carried out (Table 3). The table contains generalized information characterizing the average indicators of the chemical composition that corresponding to the coating layers. They are evaluated by statistical local spectral analysis.

The analysis results (see Table 3) confirm that the increased local heterogeneity of the sublayer is determined by the diffusion of chemical components from both the base metal (Fe, Cr) and the coating (N, O_2). The inhomogeneity of the transition layer is ~ 10 % higher than that for the obtained bands of ZrN and ZrO_2 coatings. The data obtained also confirm that there is also mutual diffusion between the coating layers. However, nitrogen and oxygen diffuse within close ranges of 2.45 and 2.89 %, respectively.

Analysis of electron microscopic photographs of the multilayer coating did not reveal significant noticeable changes at the grain boundaries.

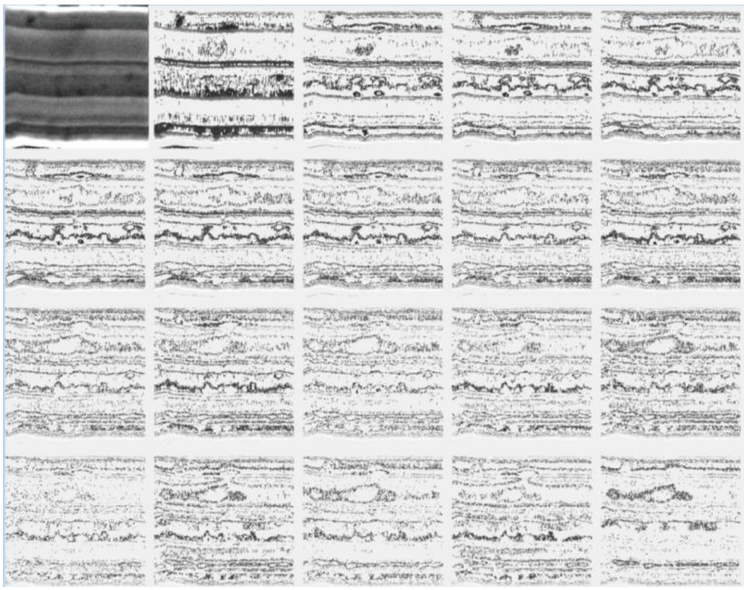
At the same time, the optical-mathematical method of analysis, based on the energy parameters characterizing the diffusion of components, the density of the analyzed fragments and dissipation, made it possible to reveal the following. In some cases, the boundaries of the transition layers are blurred, saturated with accumulations of diffusing components (compounds), or they are not ice ably thickened by inclusions.

Figure, corresponding to the 20-point estimate, shows the results of such an analysis, which describes both the state of the layer boundaries and their middle.

Table 3

Chemical composition of variability of coating layers and the degree of inhomogeneous distribution of the formed structure components

Coatinglayertype	Content of components,%				
	N	O_2	Zr	Fe	Cr
Zr	4.40	8.85	80.21	5.08...16.37 average-10.22	1.56...3.83 average-2.69
ZrN	15.0...16.0 average – 15.5	2.65...3.13 average – 2.89	80.72...82.0 average – 81.61	-	–
ZrO_2	2.31...2.66 average – 2.45	26.4...27.7 average – 26.9	69.9...71.0 average – 70.0	0.6...0.7 average – 0.65	–



Mathematical processing of the image of the multilayer coating with the identification of maximum heterogeneity by 20 points in the horizontal direction

The obtained image of the inhomogeneity is made on the basis of estimate with using dependence (2). Thismadeitpossibletoclearlyidentifythestateofthestructureandthelevelofinhomogeneitybothinsideandattheboundariesofeachlayer. The first photo (see figure) corresponds to the original image. The next 19 photos show the zones with the distribution of maximum heterogeneity, corresponding to 1/19 of the total value of the analyzed indicator.

Irrespective of the number of analyzed points, no inhomogeneity of the transition layer of zirconium with diffusion of the O_2, N, Fe, Cr components is manifested.

The description of the bands state of the multilayer coating by 19 intervals of analysis showed that, starting from 10 points, in the vertical description of structure formation, diffusion of the components from the boundaries of the ZrO_2 bands to ZrN is clearly manifested and it reaches 17 % (with respect to the cross section of the ZrN layer) in each direction. Simultaneously, when analyzing by 20 and 25 points, the structuring of the selections in the center of the ZrO_2 layers and throughout the ZrN section is also additional revealed. This process is somewhat blurred when analyzed, starting from 30 points. The boundaries of the ZrN layers are thinner and discontinuous in some zones.

As the description of structure formation by the optical-mathematical method shows, in the transition layer of the coating-base, which was applied in the form of pure zirconium, there are no inclusions, in contrast to the rest of the analyzed zones. At the same time, as shown by X-ray spectral microanalysis, the total fraction of components that are liquidating from the first layer of the coating and base into this zone reaches 19.79...35.33 %. The observed behavior is also characteristic of the boundary zones with different coatings, and the liquation of the components may also not form any compounds, but it manifests itself with their local distribution and as a quasi-homogeneous structure that evaluated by X-ray spectral microanalysis.

CONCLUSIONS

This work with using new techniques and an integrated approach by the optical-mathematical method shows the features of structure formation and the degree of inhomogeneity of the distribution of components in the coating layers. For this, the electron microscopic image of the structure was divided into 12 zones over the cross section of the multilayer coating and 19 intervals to determine the degree of inhomogeneity.

The image of the microstructures was analyzed by 2, 6, 10, 15, 20, 25, 30, and 35 points. Itwasfoundthatthemoststableresultsareachievedusing 20 and 25 points of analysis.

On the basis of this approach, the heterogeneity at the boundaries and within the grains, as well as in the Zr sublayer with the base metal, is estimated.

It is shown that the ZrN layer with the applied coating parameters contains 2.65...3.13 % O_2, and ZrO_2 – up to 2.31...2.66 % N. At the same time, the degree of inhomogeneity of these layers is quite close. Large heterogeneity is characteristic of the Zr sublayer, where it reaches 54.2%. The observed is associated with the diffusion of O_2 and N from the coating and Fe, Cr – from the base metal.

The inhomogeneity was revealed near the layers of coatings differing in composition with O_2 and N components, and in some cases, structuring inside them. The information obtained indicates about a fairly strong bond between the layers and with the base metal.

REFERENCES

1. T.S. Skoblo, S.P. Romaniuk, A.I. Sidashenko, I.E. Garkusha, V.S. Taran, A.V. Taran, N.N. Pilgui. Strengthening method for thin-walled knives with multi-layer nanocoatings and quality assessment by non-destructive method *// Journal of Advanced Microscopy Research*. 2018, v. 13, № 3, p. 333-338.

2. T.S. Skoblo, S.P. Romaniuk, A.I. Sidashenko, I.E. Garkusha, V.S. Taran, A.V. Taran, S.V. Demchenko. Study of degradation mechanism of metal-cutting tools and their hardening by ZrN PVD coatings // *Problems of Atomic Science and Technology. Series «Plasma Physics» (24).* 2018, № 6, p. 300-303.

3. A.V. Taran, I.E. Garkusha, V.S. Taran, O.I. Tymoshenko, I.O. Misiruk, S.P. Romaniuk, T.S. Skoblo , T.V. Mal'tsev. Production and characterization of CA-PVD ZrN and ZrCN coatings on AISI D3 high-carbon tool steel // *High Temperature Material Processes*. 2020, v. 24, № 2, p. 109-120.

4. I.E. Garkusha, O.V. Byrka, V.V. Chebotarev, et al. // *Vacuum.* 2000, v. 58(2), p. 195-201.

5. A. Taran, I. Garkusha, V. Taran, A. Timoshenko, I. Misiruk, V. Starikov, A. Baturin, T. Skoblo, S. Romaniuk, A.G. Mamalis. Nanostructured ZrO_2 ceramic PVD coatings on Nd-Fe-B permanent magnets // *Nanotechnology Perceptions. Switzerland*. 2019, v. 15, № 1, p.13-20.

6. T.S. Skoblo, S.P. Romaniuk, A.I. Sidashenko, V.S. Taran, A.V. Taran, I.I. Dorozhko, N.N. Pilgui. Complex evaluation of structural state degree of strengthening nanocoatings // *Problems of Atomic Science and Technology. Series «Plasma Physics» (25).* 2019, № 1, p. 225-228.

7. T.S. Skoblo, O.Yu. Klochko, E.L. Belkin. Structure of high-chromium cast iron // *Steel in translation.* 2012, v. 42, № 3, p. 261-268.

Article received 16.01.2021

ОЦЕНКА ЛОКАЛЬНОЙ НЕОДНОРОДНОСТИ МНОГОСЛОЙНОГО НАНОСТРУКТУРНОГО ПОКРЫТИЯ ZrN/ZrO_2

Т.С. Скобло, С.П. Романюк, Е.Л. Белкин, Т.В. Мальцев

Для повышения эксплуатационной стойкости деталей нанесено многослойное наноструктурное покрытие ZrN/ZrO_2. Для описания особенностей структурообразования предложен новый подход с использованием оптико-математического метода обработки металлографических изображений. Изучено структурообразование многослойного покрытия с оценкой степени его неоднородности и диффузионных процессов между слоями. Для достоверной оценки сопоставительно проанализированы изменения в горизонтальном и вертикальном направлениях изображений с выбором оптимальных интервалов. Установлено, что наиболее стабильные результаты достигаются при использовании 20 и 25 точек (пикселей).

ОЦІНКА ЛОКАЛЬНОЇ НЕОДНОРІДНОСТІ БАГАТОШАРОВОГО НАНОСТРУКТУРНОГО ПОКРИТТЯ ZrN/ZrO_2

Т.С. Скобло, С.П. Романюк, Є.Л. Бєлкін, Т.В. Мальцев

Для підвищення експлуатаційної стійкості деталей нанесено багатошарове наноструктурне покриття ZrN/ZrO_2. Для опису особливостей структуроутворення запропоновано новий підхід з використанням оптико-математичного методу обробки металографічних зображень. Вивчено структуроутворення багатошарового покриття з оцінкою ступеню його неоднорідності та дифузійних процесів між шарами. Для достовірної оцінки порівняльно проаналізовані зміни в горизонтальному та вертикальному напрямках зображень з вибором оптимальних інтервалів. Встановлено, що найбільш стабільні результати досягаються при використанні 20 та 25 точок (пікселів).