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LASER REMELTING TREATMENT OF PLASMA-SPRAYED Cr_2O_3 OXIDE COATINGS

LASEROWA OBRÓBKA PRZETAPIENIOWA POWŁOK TLENKOWYCH Cr_2O_3 NATRYSKIWANYCH PLAZMOWO

In the present paper, the influence of laser remelting on the structure and wear resistance of plasma sprayed Cr_2O_3 oxide coatings is analysed. Sprayed coatings were remelted with the use of cw- CO_2 laser. Microstructural investigations were realised with the use of an optical microscope and the SEM method. The texture and phase composition of the coatings were defined with the help of the diffraction method. In addition, the influence of remelting on the wear resistance of plasma sprayed coatings was assessed. The results achieved during the realisation of this work have confirmed the effectiveness of the applied surface treatment, which was expressed by beneficial changes in the structure and the properties of Cr_2O_3 oxide coatings.

Keywords: plasma-sprayed coatings, chromium oxide, surface remelting treatment

W pracy dokonano analizy wpływu laserowego przetapiania na strukturę i odporność na zużycie powłok tlenkowych Cr_2O_3 natryskiwanych plazmowo. Powłoki natryskiwane zostały przetopione przy użyciu lasera CO_2 o ciągłej charakterystyce pracy. Badania mikrostrukturalne realizowano za pomocą mikroskopu optycznego i metody SEM. Teksturę i skład fazowy powłok określono za pomocą metody dyfrakcji rentgenowskiej. Dokonano ponadto oceny wpływu obróbki przetopieniowej na odporność na zużycie powłok natryskiwanych plazmowo. Uzyskane w ramach pracy rezultaty potwierdziły skuteczność zastosowanej obróbki powierzchniowej, czego wyrazem były korzystne zmiany w strukturze i własnościach powłok tlenkowych Cr_2O_3 .

1. Introduction

Continuous pursuit of the increase in durability and reliability of machines and devices forces the application of ever newer manufacturing methods and technologies, as well as technologies of material modification. Very often these technologies are from the field of material engineering. Such technologies enable regenerating worn out parts or contribute to the increase of their operational parameters, thanks to which the product is able to fulfil the increasingly higher requirements that are set by the users.

In the group of surface technologies a key role is played by thermal spraying. Generally speaking, the role of this process comes down to the creation of protecting coatings on the product surface with the desired composition and properties. Considering the sources of heat energy used for melting sprayed coating material, spraying is divided into gas thermal spraying, plasma spraying, detonation spraying, and others [1-3].

Plasma spraying method (APS – Atmospheric Plasma Spraying) is one of basic methods of the coating

processing by virtue of many advantages coming from the nature of this process. These include a broad range of deposited materials (metals, ceramics, even polymers) with little impact on the properties of the substrate material, as well as simple and fast process realisation. Among the coating materials, the most often applied are the powders of metals and oxides. One of such coating materials is chromium oxide (Cr_2O_3), which is characterised by a high melting temperature (2435°C), good mechanical properties, and high resistance to the influence of corrosive factors. On the other hand, the disadvantages of the APS method include the porosity of the coating, in a range of 2-15% (unfavourable especially in case of anticorrosive coatings), segregation and in many cases too low adhesion to substrate material resulting, among others, from thermal stresses that are generated in the coating [4-11].

However, the properties and composition of plasma sprayed coatings can be improved by the remelting of a thin surface layer with the use of high energy heat sources. Remelting treatment and accompanying rapid

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crystallisation can lead to the decrease or elimination of characteristics that are typical for the applied manufacturing method. As a consequence, it provides the possibility of achieving more homogenous coatings with lower porosity and a laminarity free structure, or can contribute to the constitution of layers with completely different properties [12-15].

2. Material for investigations

The investigated material was in the form of Cr_2O_3 oxide coatings deposited on a metallic substrate by plasma spraying. The powder used was commercially available Cr_2O_3 (AMIL Werstofftechnologie GmbH) with a granulation of $63 \pm 16 \mu\text{m}$. A Cr_2O_3 powder structure is shown in Fig. 1. Substrate was X5CrNi18-10 steel in the form of rectangular prism samples with dimensions of $70 \times 30 \times 6 \text{ mm}$. The chemical composition of X5CrNi18-10 steel is shown in Table 1. Prior to plasma spray deposition, the substrates were cleaned and grit-blasted with silicon carbide particles to enhance coating adherence and to remove any surface contaminants. Additionally, bonding layer consisting of composite powder Ni-Al deposited on a metallic substrate, was applied. Both bonding layers and Cr_2O_3 coatings were deposited with the use of a PN120 plasma set manufactured by ZDAU-IBJ. The following process parameters were set: $I = 550 \text{ A}$, $U = 65 \text{ V}$, distance from substrate 120 mm .

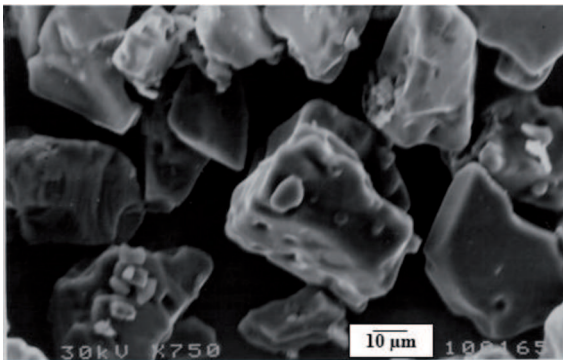


Fig. 1. Structure of the Cr_2O_3 powder used in the plasma spraying process, SEM

TABLE 1
The chemical composition of X5CrNi18-10 steel (wt.%)

	C	Mn	Si	P	S	Cr	Ni	W	Cu
X5CrNi18-10	0-0.07	0-2	0-0.8	0-0.045	0-0.03	17-19	9-11	–	–

A continuous-wave CO_2 laser with a wavelength of $\lambda = 10.6 \mu\text{m}$ and a maximum power output of 1.3 kW ($\pm 4\%$) was used. The power output was 824 W . The

beam size was adjusted by varying the distance between the sample and the focusing lens. The assumed process parameters are shown in Table 2.

TABLE 2
Parameters of Cr_2O_3 coating remelting

No.	Distance of the focal point from the surface df (mm)	Scanning speed V (mm/s)	Laser power Q (W)	Laser Power per area unit (kW/cm^2)	Bandwidth W_p (mm)
1	30	6.3	824	4.4	3.45-3.65
2	30	10		4.4	3.15
3	30	16.7		4.4	2.95
4	30	33.3		4.4	3.95
5	24	8.7		6.4	3.0
6	24	12		6.4	2.25-2.8
7	24	16.7		6.4	2.75
8	24	33.3		6.4	3.0
9	16	12		15.4	2.15-2.3
10	16	8.7		15.4	1.9
11	16	25		15.4	2.25
12	16	33.3		15.4	2.25-2.35

The laser beam was focused on the specimen by means of ZnSe lens. A protective atmosphere of argon gas was maintained to prevent oxidation. The track dimensions and the effects of laser processing on the plasma-sprayed coating microstructure were regulated by both scanning rate and distance of the specimen from the laser beam focus. The scanning velocity was contained within the range from 6.7 to 33.3 mm s^{-1} , while the distance from the focus, “ df ”, was set at 16 - 30 mm (Tab. 2).

In order to establish the optimal parameters of the process series of tests with varied sample scanning velocity and distance from the focus have been carried out.

3. Research methodology

The quality of the produced coatings was assessed basing on macro- and microscopic observations, as well as on the X-ray analyses connected with a texture investigation. Tribological tests were also performed.

Structural analyses had a comparative character for confronting the as-sprayed coatings and the laser remelted ones. Both surfaces of the obtained strips and their cross-sections were taken under observation. They were realised with the use of a JEOL JSM-5400 scanning electron microscope. A scanning survey was performed by means of light microscopy using an Axiovert 25 micro-

scope. Samples for microscopic investigations were prepared in a traditional way by grinding them on abrasive paper and polishing them with diamond paste. Samples were analysed in a non-etched state.

Phase composition investigations of oxide coatings and Cr_2O_3 powder were carried out using a Seifert XRD-3003 X-ray diffractometer, which utilises the radiation of a copper lamp ($\lambda = 0.15418 \text{ nm}$). The defined operational parameters of the diffractometer are shown in Table 3. Texture measurement was carried out with the use of a TSA-3 attachment. In the experiment, a reflexive technique was utilised. In order to achieve high precision, which is indispensable for visualising a pole figure, special attention was paid to the proper preparation of a sample for the investigations. Therefore, those samples that exhibit representative characteristics for a given material were selected for texture analysis. The possible texture inhomogeneity in the material and a relatively small penetration depth of X-rays were taken into account in the considerations.

TABLE 3
Compilation of X-ray diffractometer operating parameters

U_{lamp} (kV)	I_{lamp} (mA)	U_{detector} (V)	Angular range	Angular step	Time of impulse counting (s)
40	30	930	α (0-75°) β (0-360°)	α (5°) β (15°)	5

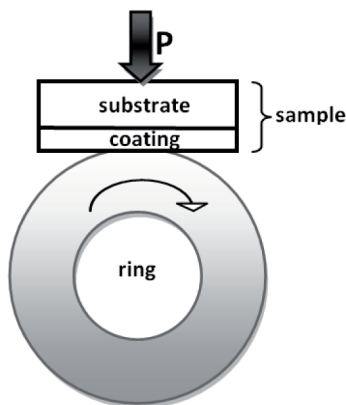


Fig. 2. Diagram illustrating the course of the tribological investigations

Tests of the wear resistance were conducted with the use of a T-05 block-on-ring type laboratory tester (Fig. 2). The investigations were realised under unlubricated sliding contact against the steel ring (HRC 58-63) with the application of a sample with a flat friction area. The tests were run at the constant normal load of 200 N and sliding velocity $\sim 0.5 \text{ m/s}$. The wear resistance was determined by measuring the weight losses of the samples after a certain time interval with a precision of

$\pm 0.00001 \text{ g}$. Prior to the test, the surface of the coating was polished. Investigations covered a series of samples before and after laser treatment.

4. Results and discussion

4.1. Macroscopic investigations

Macroscopic investigations of the remelted layers revealed significant differences, both qualitative and quantitative, in the characteristics of particular bands (Fig. 3), resulting from the application of various remelting parameters. The assessment of variations in the effect of the laser beam influence in the function of process parameters enabled the detection of a series of regularities that are significant from the functional point of view. The most favourable changes from a macroscopic point of view were registered in case of bands 7, 8, 11, and 12 remelted at $V=16.7\text{-}33.3 \text{ mm/s}$ and $df=16\text{-}24 \text{ mm}$. Lower scanning speed led to the appearance of considerable cavities in the analysed material, which deprived the layer of application value. On the other hand, at the values of $df = 30 \text{ mm}$ hardly any effects of remelting with the use of the laser beam were noticed. After remelting, decohesion of the layers or any other alterations that could disqualify the applied processing methodology were not found.



Fig. 3. Macroscopic effects of remelting

The analysis of the remelted bandwidth in the function of remelting parameters enabled the observance of some correlations and relationships. Namely, it was found that the increase of the remelting zone takes place together with the increase of the df value. A less distinctive relationship was noticed in the case of correlating the W_p parameter values with the scanning speed V . An increase of the bandwidth with a decrease of the scanning speed were observed. Such regularity was not proven in all of the realised remelting, however. The reason for such could be the impossibility of a precise definition of the remelting border, which in consequence led to the underrating or overrating of the W_p value.

4.2. Microstructure of coatings

Research in the scope of light microscopy and scanning electron microscopy revealed properties in the sprayed layers that are characteristic of a given manufacturing method. The character of sprayed coatings is shown in Fig. 4. Laminar structure and considerable porosity located mainly in the spaces between the contacting layers of solidifying material are especially visible. Inhomogeneity, which is typical for sprayed coatings

and manifests itself by e.g. the presence of particles of various remelting degree, was also found.

The observations of remelted coatings revealed considerable differences in the composition and structure of the Cr_2O_3 layer in relation to its equivalents (Fig. 5). In the remelted layers, the condensation of coating material was noticed, which manifests itself by the disappearance of the laminar structure and a considerable decrease of porosity. Simultaneously with the disappearance of pores, the process of spheroidisation and coalescence of

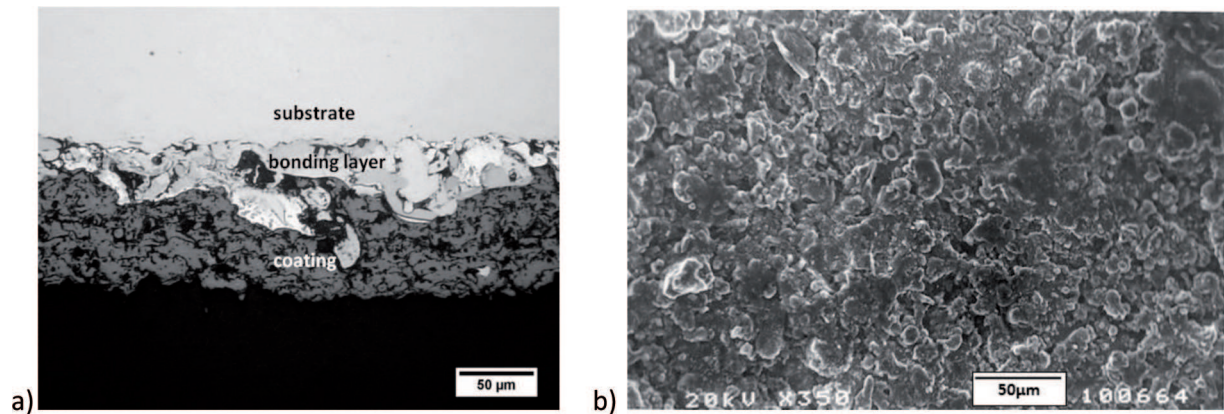


Fig. 4. Structure and morphology of plasma sprayed coatings: a) cross-section – light microscope and b) surface, SEM

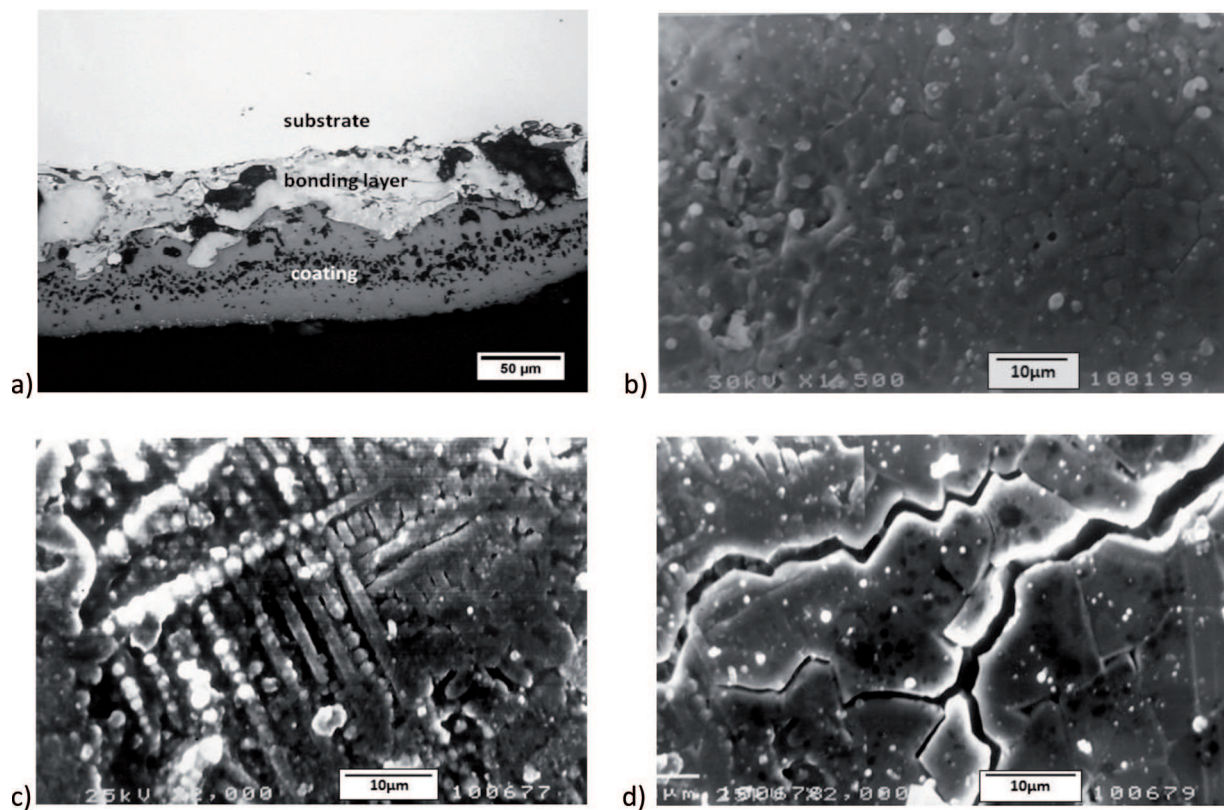


Fig. 5. Structure and morphology of coatings after surface remelting treatment: a) cross-section – light microscope and b-d) surface, SEM

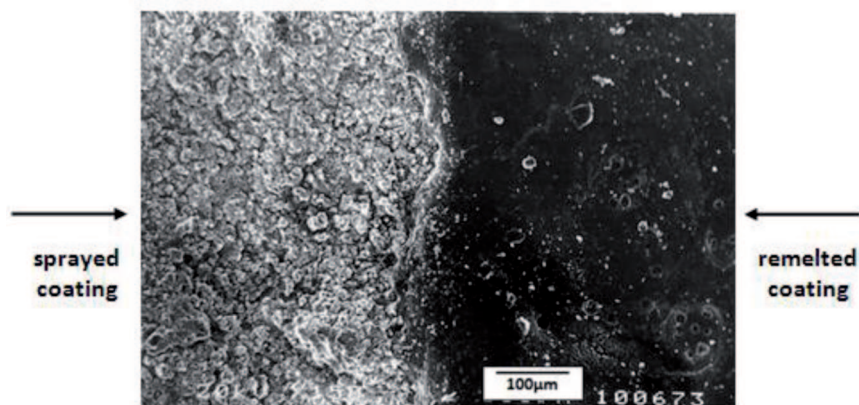


Fig. 6. Border between the sprayed and remelted surface (SEM)

pores also created in the layer is observed. In addition, an important element was the homogenization of the coating composition. The influence of the laser beam led to the creation of a fine dispersed structure with diverse morphology of phases. In the majority of the obtained research material dendritic and cell-dendritic structures prevail, which are a result of the assumed remelting parameters (Fig. 5c). Ultra fast heating and solidifying, which accompanies laser processing, can cause the loss of coherence in the solidifying material. A presence of a few micro fractures was discovered in remelted layers, but this property does not deprive the coating of its functional characteristics (5d).

The nature of the changes (also in the geometric structure of the surface), which took place in the Cr_2O_3 oxide coatings obtained by means of plasma spraying and following laser remelting, is clearly shown in Fig. 6.

4.3. Investigations of phase composition

Investigations of the phase composition were conducted on each stage of introducing modifications according to the sequence: powder – sprayed coating –

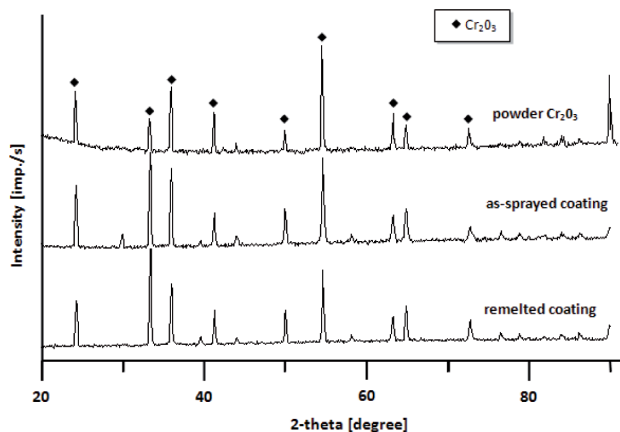


Fig. 7. Results of the X-ray phase composition analysis of the powder, sprayed coating and remelted coating

remelted coating (Fig. 7). Based on the obtained results, no significant changes in the phase composition of the analysed coating material were found. Moreover, it was proven that in the range of the applied remelting parameters, the phase composition of coatings is not a result of these parameters (Fig. 8). The obtained results prove the high stability of Cr_2O_3 oxide on spraying conditions, as well as on subsequent remelting.

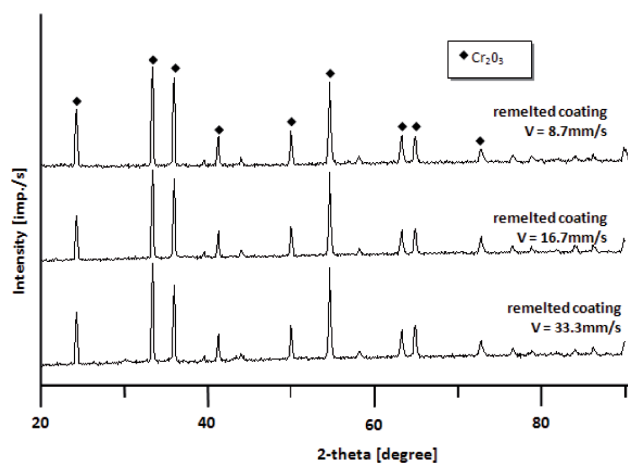
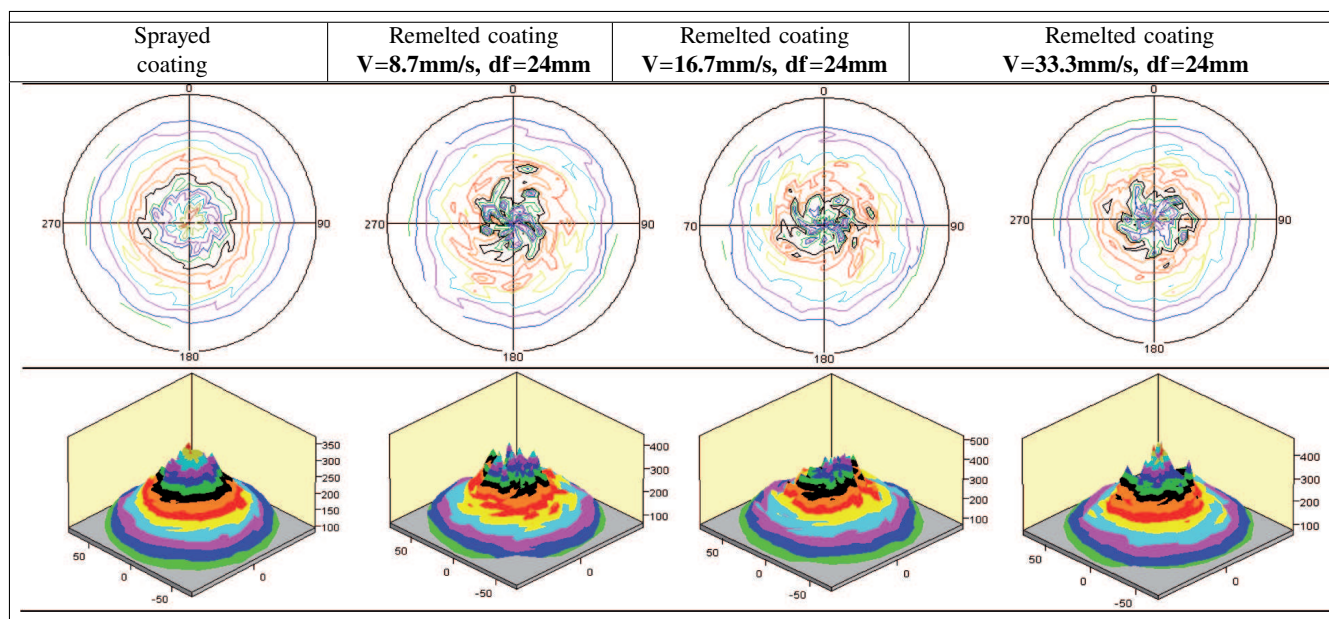


Fig. 8. Results of the X-ray phase analysis of oxide coatings as a function of applied remelting parameters

4.4. Texture of Cr_2O_3 coatings

A successive stage of the research was the analysis of texture, which includes both plasma sprayed and remelted coatings. The term “texture” defines a phenomenon of a privileged orientation of crystals in polycrystalline material. Knowledge about the above problem plays an important, practical role because the presence of texture influences, among others, the anisotropy of many material properties. The causes of its occurrence in sprayed coatings include crystallisation, plastic deformation of sprayed particles or possible phase transitions. Conducted investigations of the phase composition

Pole figures of sprayed and remelted coatings



prove the stability of the coating material composition along consecutive phases of modification allowed the rejection of the last cause. Texture investigations of the sprayed and remelted coatings showed the presence of a distinguished orientation of crystals (Table 4). Therefore, the original assumption that a coating in the plasma sprayed state will not exhibit any privileged orientation was not confirmed in this case. It can be presumed that a possible cause of the appearance of a distinguished orientation was the rapid crystallisation of the coating material. The obtained pole figures were characterised by a distinctly symmetric location of diffraction reflections from structure planes around the centre of the pole figure. The recorded symmetry of pole figures, as well as the course of isolines, proves that a weak fibrous texture formed in the investigated coatings. More insightful analysis of pole figures obtained from remelted coatings allows the identifying of some differences expressed by a larger concentration of lattice plane poles and a superior presence of local maximums in relation to analogous sprayed layers, which can be attributed to the homogenisation of the coating material and changes in the layer structure. However, the influence of remelting parameters on the character of pole figures was not observed. It is, therefore, possible to state that in the scope of the used processing parameters, the character of the material texture did not undergo any significant changes. In Table 4, the pole figures were sprayed and remelted with the use of variable scanning speeds in the range of 8.7-33.3 mm/s, and the coatings were compiled and compared.

4.5. Investigations of the tribological properties of Cr_2O_3 coatings

Favourable changes of the composition and structure of the sprayed and remelted coatings compared to their only sprayed equivalents, revealed during the microstructural investigations, allowed for the expectation of the acquisition of equally positive results of the tribological tests. The obtained results confirmed the correctness of such assumption, which is proven by the characteristics shown in Fig. 9, which presents the mass decrement of

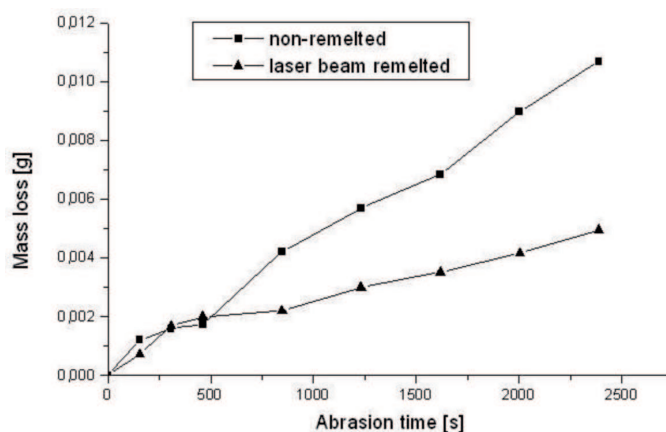


Fig. 9. Results of the tribological tests of the investigated oxide coatings

the investigated Cr_2O_3 layer in the function of abrasion time. Distinctive improvement of the layer's mechanical properties after remelting, resulting in considerably lower mass decrement, is the most interesting property of the presented characteristic. In relating the obtained

tribological characteristics to the structure and composition of the remelted layer it can be stated that the improvement of the mechanical properties of the remelted layers was mainly the result of the refinement of the structure, decrease of the porosity, and homogenisation of the coating material.

5. Conclusions

The results that were obtained during the course of the conducted research allow for the formulation of the following important conclusions:

1. Proper control of laser treatment parameters enables achieving satisfying microscopic structure and macroscopic features. The most favourable modifications in the analysed coatings were found when the following process parameters were used: $V = 16.7\text{-}33.3$ mm/s and $df = 16\text{-}24$ mm.
2. The quality of the laser remelted coatings finds its reflection in the changes generated in the structure compared to the only sprayed equivalents. Remelted coatings are distinguished by decreased porosity, the disappearance of structure laminarity, and the higher homogenisation of the coating material.
3. X-ray phase analysis proved the stability of the phase composition of the examined material in the function of the tested remelting parameters.
4. The rapid crystallisation phenomenon was a possible factor influencing the formation of a weak fibrous texture in both sprayed and remelted layers. The obtained pole figures were characterised by a symmetric distribution of diffraction reflections with an accented figure centre.
5. Tribological tests proved the advantage of the applied laser treatment through the increase of wear resistance. The mass decrement recorded during the experiments was considerably lower compared to the only sprayed layers.

6. Laser remelting treatment is an effective method leading to the limitation or elimination of flaws and imperfections occurring in sprayed coatings.

REFERENCES

- [1] A. Pokhmurska, R. Ciach, Surf. Coat. Technol. **125**, 415 (2000).
- [2] S.O. Chwa, A. Ohmori, Surf. Coat. Technol. **148**, 88 (2001).
- [3] A. Klimpel, Napawanie i natryskiwanie cieplne, Wyd. Naukowo-Techniczne, Warszawa 2000.
- [4] J.M. Cuetos, E. Fernández, R. Vijande, Wear **169**, 173 (1993).
- [5] A. Cellard, V. Garnier, G. Fantozzi, G. Baret, P. Fort, Ceram. Int. **35**, 913 (2009).
- [6] H. Cetinel, E. Celik, M.I. Kusoglu, J. Mater. Process. Tech. **196**, 259 (2008).
- [7] R. Krishnan, S. Dash, C. Babu Rao, R.V. Subba Rao, A.K. Tyagi, B. Raj, Scripta Mater. **45**, 693 (2001).
- [8] Y. Yuanzheng, Z. Youlan, L. Zhengyi, Ch. Yuzhi, Mater. Sci. Eng. A **291**, 168 (2000).
- [9] Z. Nitkiewicz, Wykorzystanie łukowych źródeł plazmy w inżynierii powierzchni, Wyd. Wydziału Metalurgii i Inżynierii Materiałowej Politechniki Częstochowskiej, Częstochowa 2001.
- [10] L. Sun, C.C. Berndt, C.P. Grey, Mater. Sci. Eng. A **360**, 70 (2003).
- [11] J. Iwaszko, Kształtowanie struktury i składu fazowego przetapianych powłok tlenkowych ZrO_2 i Al_2O_3 , Wyd. Politechniki Częstochowskiej, Częstochowa 2008.
- [12] C. Chen, D. Wang, Q. Bao, L. Zhang, T. Lei, Appl. Surf. Sci. **250**, 98 (2005).
- [13] P. Jiang, X.L. He, X.X. Li, L.G. Yu, H.M. Wang, Surf. Coat. Technol. **130**, 24 (2000).
- [14] J. Iwaszko, Surf. Coat. Technol. **201**, 3443 (2006).
- [15] J. Mateos, J.M. Cuetos, E. Fernández, R. Vijande, Wear **239**, 274 (2000).