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Surface modification of ZrO_2-10 wt. % CaO plasma sprayed coating

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Abstract. Oxide ZrO_2-CaO plasma-sprayed coatings were remelted using the modified gas tungsten arc welding (GTAW) method. The original two-burner set, generating a free independent arc, was used in the treatment. The samples were subjected to structural examination using light and scanning electron microscopes, and energy-dispersive X-ray microanalysis (EDX). A substantial heterogeneity of the plasma-sprayed coatings was found, observable with a laminar structure, significant porosity, and step change in the concentration of the elements. Significant changes in the structure were found after the remelting treatment. Both microscopic and EDX investigations showed that the treatment leads to a reduction in the heterogeneity of the chemical composition of the coating material and to a loss of structural characteristics typical for plasma-sprayed coatings.

Key words: remelting treatment, GTAW method, oxide coating.

1. Introduction

The modification of the surface layer of engineering materials by means of concentrated sources of heat represents one of the most important branches of surface engineering. The application of a laser beam, plasma flux, or electron beam results in rapid crystallisation, which accompanies the operation of the material's surface layer formation, and hence, the structure is formed under conditions of a high temperature gradient and a very short duration of coagulation. An indirect consequence of rapid crystallisation may be the increase of hardness, improvement of tribological properties, resistance to corrosion, etc. The surface layer modification is generally carried out by means of a laser beam. Laser beams, due to their high coherence and directionality, are utilised in treatment of a very wide range of engineering materials [1–7]. An alternative solution to laser, plasma, or electron beam techniques seems to be the gas tungsten arc welding (GTAW) method. In this method, the heat source is an arc within an inert gas shield, which burns between an infusible electrode and the remelting agent. The gas shield used in the GTAW method protects the molten pool against interaction with atmospheric air, which is particularly vital in the case of treatment of materials showing a strong affinity to oxygen or nitrogen. The shielding gas also influences the arc linear energy, as well as the shape of the remelting band and the dimensions of the remelting zone. In turn, the proper selection of current-voltage parameters and scanning speed provides a potential possibility for shaping the remelting zone dimensions and inducing desirable structural changes in the material. Taking into account the prevalence of welding equipment, the facility of process implementation, and the low cost of equipment and supplies, the GTAW method seems to be an interesting alternative to laser, plasma, or electron beam techniques. The effectiveness of the GTAW method in the process of modification of the surface layer has been confirmed in, among others, [8–11]. However, the GTAW technique is rarely used in surface engineering. This is partly due to common beliefs and stereotypes, according to which, welding methods are useful only in cases of joining of materials. It is true that the implementation of welding techniques in the surface layer modification process of some materials is connected with the necessity of solving methodical problems resulting from the physicochemical and thermoelectric properties of the remelting material. This is due to the fact that in the GTAW method the electric arc burns between an infusible electrode and a remelting surface. Therefore, in the case of the material being an insulator and the arc ignition and its stabilisation being hindered or impossible, the surface remelting processing requires a modification of the welding stand and the remelting methodology itself. This study contains an example of the solution, which enables one to overcome such methodological and instrumentation problems occurring during the remelting treatment of non-conductive, plasma-sprayed coatings. The methods of thermal spraying, which are representative of plasma spraying, give rise to the possibility of application of a wide range of coating materials to metallic, ceramic, and even polymeric substrates [12, 13]. The significance of application of sprayed coatings is unquestionable. However, due to the substantial porosity, heterogeneity, and the laminar nature of the structure of thermally-spread coatings, more and more often, additional treatment modifying the structure and properties of those coatings is carried out [14–17]. As a part of this study, a remelting treatment of ZrO_2-CaO oxide plas-

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ma-sprayed coatings was performed, and for the remelting of the coatings, the GTAW method was used. The plasma-sprayed ZrO_2 oxide coatings, stabilized by CaO oxide or other stabilizers, are applicable when resistance to oxidation, erosion, wear and corrosion is required. These coatings are used extensively as thermal barrier coatings (TBC) for high-temperature applications, such as gas turbines, diesel engines, and other engine components. The plasma-sprayed ZrO_2 oxide coatings make it possible to significantly reduce the surface temperature of the elements they protect, which results in longer product life and increased operational efficiency. The choice of substrate for the plasma-sprayed ZrO_2 coating depends on the application of the part coated by stabilized zirconia. Therefore, ZrO_2 coatings are formed on a variety of substrates, e.g. nickel superalloy substrates, aluminium alloys, tool steels, stainless steels, valve steels, and others. In many applications, the zirconium dioxide coatings are deposited on X5CrNi18–10 steel, and that was the main reason for using this substrate in the experiment.

2. Experimental

The ZrO_2-CaO oxide coatings made by the plasma-spraying method on X5CrNi18–10 steel samples were treated by the surface remelting method. The plasma-sprayed coatings were obtained by the use of the PN-120 set (ZDAU-IBJ, Poland). ZrO_2 powder with an addition of 10 wt. % of CaO was used (Amperit 803 by H.C. Starck). To increase the adhesion of the ceramic coating to the substrate, the bonding layer was made of Ni-Al (80/20) composite powder (AMI 3412 by AMIL Werstofftechnologie Gmbh). Prior to plasma spray deposit, the substrates were cleaned and sandblasted with silicon carbide particles to enhance coating adherence, and to remove any surface contaminants. The spraying distance was 130 mm. The thickness of the layers obtained varied between 200–250 μm. Due to the lack of electrical conductivity of the oxide material, it was necessary to introduce changes to the construction of the welding stand and treatment methodology. The tests carried out, supported by the conceptual and construction changes, showed that the correct remelting effect could be obtained after the application of the dual-torch system, which generates a free, independent arc. The modified material is, therefore, a "passive" receiver of heat emitted from the electric arc which burns between two infusible electrodes, making the treatment operator independent of the material's properties. To obtain a free independent arc, it was necessary to equip the torch with a pair of infusible electrodes (at least one), the first of which was connected to the negative pole on the power supply, and the second one to the positive pole on the source. The graphical representation of this solution is presented in Fig. 1a. The welding station is presented in Fig. 1b. The technical details of the solution developed are presented in [8, 18]. The remelting was carried out by applying a DC current. Electrodes with different diameters (4 mm and 2.4 mm) were used, conditioned by their polarity. To increase the thermal resistance of the electrode with positive polarity, an electrode of such a diameter was used, so that its heat capacity would be sufficient to absorb the heat generated by the arc, without melting it. Such is the case, since it is recommended that the diameter of the EP positive electrode is at least twice as large as those recommended for single-electrode welding using an alternating current (AC) for the assumed current loads (within this study, the diameter of the positive electrode was 4 mm for a current of up to 70 A). In addition, to increase the durability of the positive electrode, its tip was rounded, whereas the tip of the electrode with negative polarity was sharpened. This solution additionally stabilized the arc during the melting. The optimum inclination angle of the additional electrode was established experimentally on the basis of macro- and microscopic investigations, including assessment of the coating surface and measurements of the remelted band and the depth of the remelted oxide layer. During the tests, it was also found that increasing the angle between the burners leads to increased instability of the arc, the consequence of which were unfavourable changes in the geometric surface. What is more, the increase in the

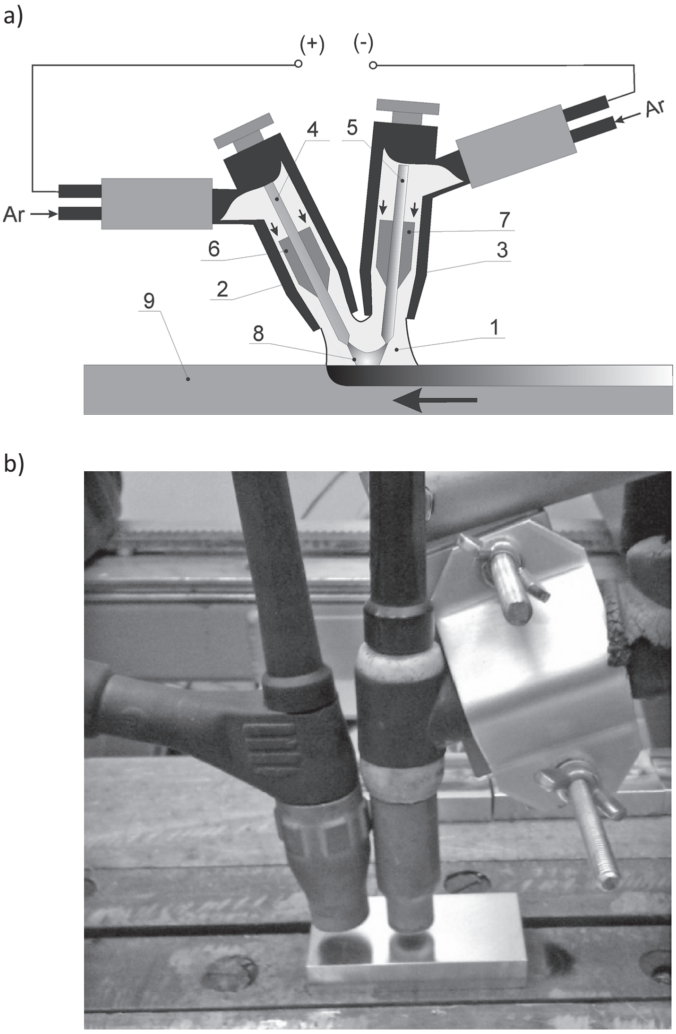

Fig. 1. The method of oxide coating treatment: 1 – Shield gas, 2, 3 – Gas nozzles; 4, 5 – Infusible electrodes; 6, 7 – Current contact; 8 – Independent electric arc; 9 – Remelted sample

angle between the burners led to a higher arc diffusion, and by this, to its lower stability. In turn, the reduction in the angle between the burners, which gives a more focused arc, increases the depth of the melting.

Shielding gas flow was set at 8 $dm^3 \cdot min^{-1}$ (the argon blast intensity was conditioned by the current intensity). Shielding gas flow in the additional torch was fixed at 14 $dm^3 \cdot min^{-1}$. The distance between the electrode tips and coating surface was approx. 3 mm, and the distance between the electrodes was approx. 5 mm. The treatment was performed with the welding current from 45 up to 70 A, and the speed of sample movement from 5.4 up to 8.7 $mm \cdot s^{-1}$.

The structural observation was carried out with the use of an Olympus GX41 microscope and a JEOL JSM 5400 scanning electron microscope. For the SEM tests, the analysed samples were coated with a conductive layer of carbon. Making metallographic microsections required taking into account the specific properties of plasma-sprayed coatings. The porosity of the layer, the fragility of the coating compound, the heterogeneity of chemical composition, the differences in hardness of the individual components – all of these factors made it difficult to obtain microsections of a satisfactory quality. In particular, a serious problem was the possibility of decohesion and delamination of the layer during grinding and polishing. The effects of decohesion and delamination were observed, and what is more, this was despite having the samples mounted in resin. It was found that the occurrence of the abovementioned phenomena was particularly affected by the direction of the rotation of the polishing / grinding disk in relation to the position of the layer on the substrate. In Fig. 2, the forces acting on the coating during the creation of the microsection are presented versus the direction of the disk rotation. For the case presented in Fig. 2b, the effect of decohesion of the layer as well as its delamination was often observed. Due to this, all samples were ground and polished according to the variant in Fig. 2a. The polished samples of both as-deposited sprayed coatings and the laser remelted tracks were also analysed using a JEOL JSM-5400 scanning electron microscope, equipped with energy-dispersive X-ray microanalysis (EDX). The investigations included linear distributions of the radiation characteristic for individual chemical elements.

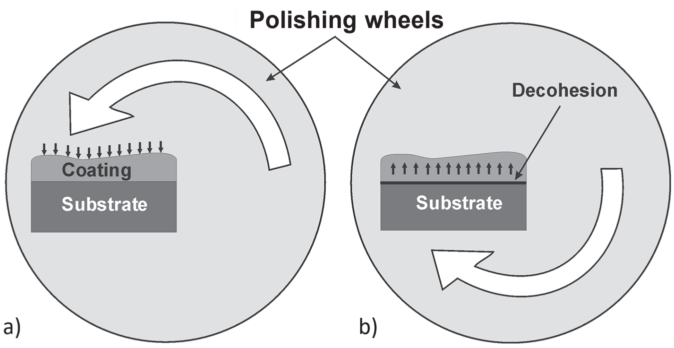

Fig. 2. The direction of grinding and polishing of the metallographic microsections

3. Results and discussion

The microstructural investigations have demonstrated that the best remelting effects occur with the application of the welding I current rated from 48 up to 55 A, and the scanning V speed of between 7.8 and 8.7 $mm \cdot s^{-1}$. In the samples subjected to remelting within the parameters referred to above, it was found that both the porosity of the structure and the lamination disappear at the same time, with acceptable changes in the geometrical structure of the substrate. With the current below 48 A, the absence of the remelting effect was observed, whereas with the current above 60 A, the treatment was accompanied by adverse changes in the surface geometry, including the displacement of the melted coat compound to the outside of the area of the arc's effect. These changes were, to a lesser extent, a function of the movement speed of the heat source.

Demonstrative examples of macroscopic effects of the remelting of oxide coatings using the GTAW method are shown in Fig. 3 as a function of applied parameters.

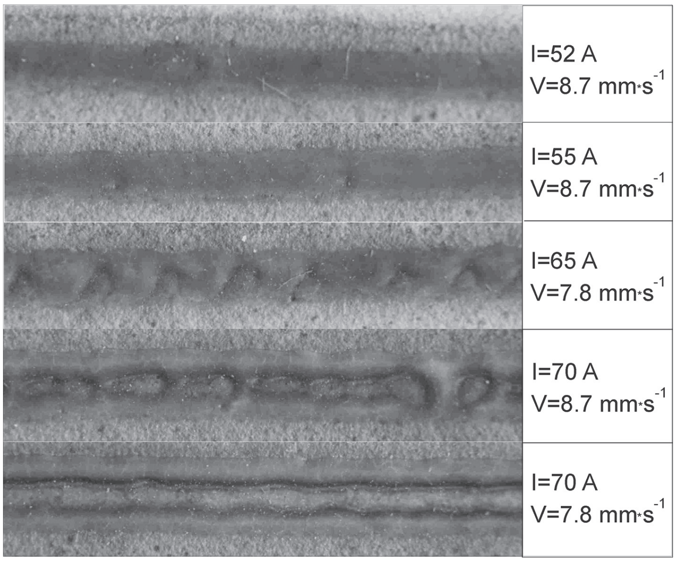

Fig. 3. Macroscopic effects of the remelting of ZrO_2-CaO coatings

The analysis of the plasma-sprayed coatings revealed a number of features typical for the technique used, i.e. structure lamination with lamellae aligned in the plane of the substrate and significant porosity occurring predominantly in spaces between the contact layers of the solidifying material. The scanning electron microscope examination also showed a localised presence of both superficially melted and non-melted particles.

An example of a structure in the state after spraying is presented in Fig. 4a and 4b.

In the coatings subjected to the remelting treatment, favourable changes in both the structure and the construction of the oxide layer were found. The remelted coatings were characterised by a clearly reduced porosity, whereas the few-remaining pores in the coating underwent spheroidisation. The layered

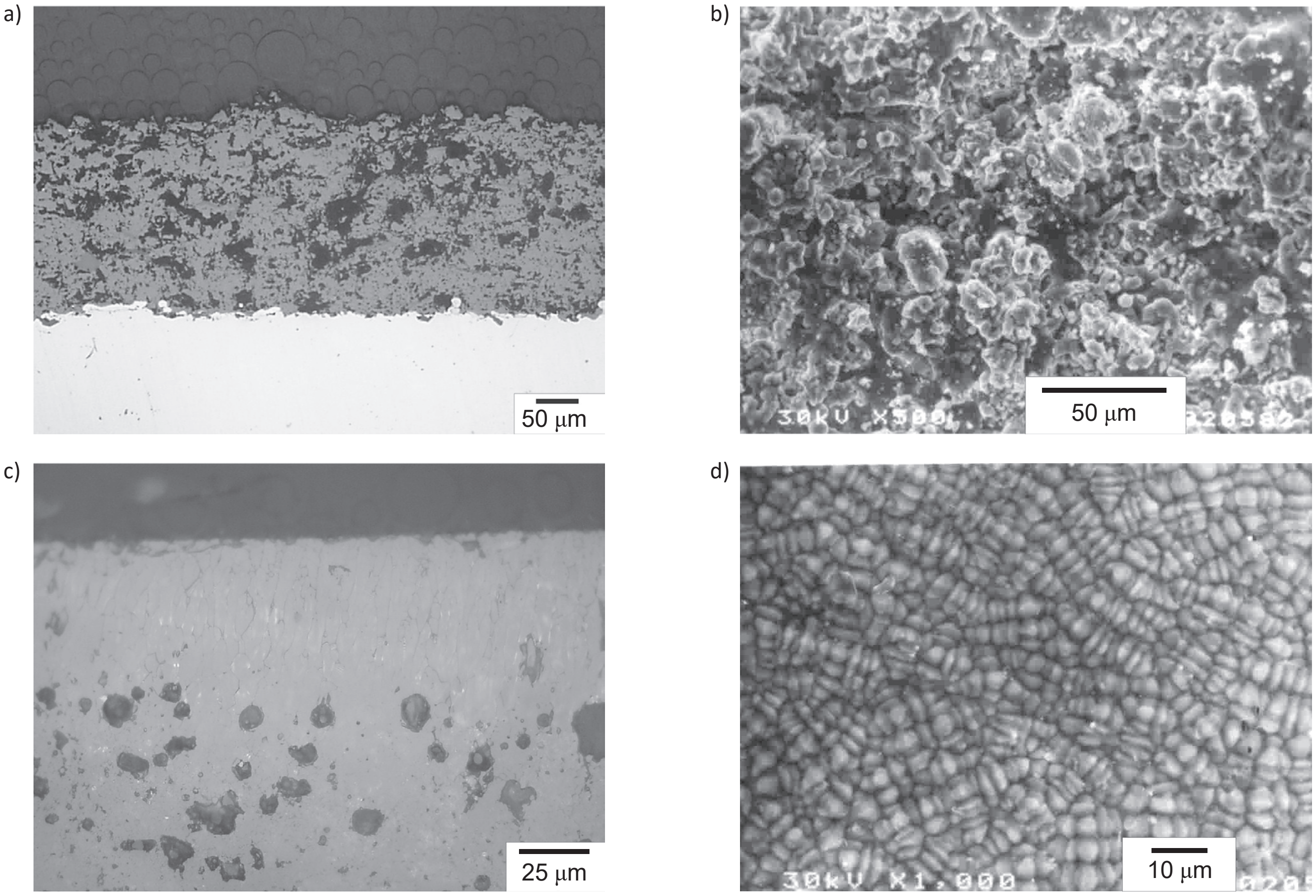

Fig. 4. The structure of the sprayed coating (a, b) and the remelted coating (b, c). Coating surface (b, d), cross section (a, c). Light microscope (a, c), SEM (b, d)

coating character, typical for plasma sprayed layers, was completely removed. In addition, an intensive refinement of the structure, and an evident homogenisation of the material were found. In the remelted layers, both microdendritic and cell-dendritic structures prevailed. In Fig. 4c and 4d, the typical structures of the remelted coatings are presented.

It should be noted that both the character of obtained structures and the thickness of remelted part were the result of treatment parameters. Thusly, the flexible modelling of quantative correlation between remelted and non-remelted parts was possible, with a complete elimination of the porous part. Shortening of the time of impact of electric arc with oxide layer surface led to the disappearance on the non-remelted part. A decrease in the scanning velocity, in correlation with an increase of the welding current, allowed to increase the remelted zone, up to a complete remelting of the oxide layer.

The phenomenon of rapid crystallization, that accompanies both plasma spraying and remelting, is a factor conducive to formation of many new compounds, in particular non-equilibrium structures and phases. In the case of ZrO_2-CaO coatings, changes in polymorphic forms of the ZrO_2 are possible, in spite of the presence of the CaO stabilizer. Additionally, a partial degradation of the stabilizer or its burnout may occur, which then makes it impossible to totally eliminate the presence of any disadvantageous monoclinic crystal form. The phase aspects will be presented in another paper.

The EDX investigations carried out within this study were aimed at the simulation of the nature of the plasma sprayed layer and the illustration of the changes produced in the material subjected to a high-temperature treatment. The results of the EDX analyses are presented in graphical form in Fig. 5. The EDX investigations of plasma-sprayed coatings showed their significant heterogeneity, demonstrated by an abrupt change in the concentration of individual chemical elements included in the coating. The rate and extent of these changes is clearly visible in Fig. 5 (Zone A). Taking into consideration the characteristics of plasma spraying, and the mechanism of the "growing" of the layer, the above state is fully explicable. It comes about, because this method involves risking a mere partial surface melting of the powder, which hinders obtaining a chemically homogeneous material. Admittedly, this can be prevented by extending the time the powder remains in the plasma arc, but in turn, this involves the risk of burning up the oxide stabilizer and the occurrence of an undesirable phase transformation of ZrO_2. The results of the EDX investigations prove that the mixture of oxides used for testing the investigated layers did not melt in the plasma arc enough to prevent macroscopic heterogeneity of the layer. The proof for this is not only the clear-cut interface observed, dividing the areas where the individual components of the coating were present, but also the shape of the sprayed particles, found during the SEM investigation, which often maintained their original spherical form. Therefore, the presence of clear "islands" with linear distributions, i.e. the places with an increased concentration of the individual chemical elements, has a logical explanation. A different distribution of the concentration of the chemical elements, in relation to the material being sprayed, was found in the layers subjected to the remelting treatment. The rate and the extent of these changes can be seen clearly in Fig. 5 (Zone B). First of all, a better, even spread of the concentration of the individual chemical elements was found. Among other things, an abrupt change in the concentration of the individual chemical elements, so characteristic for sprayed layers, was not present. Therefore, the statement that the remelting treatment and the rapid crystallisation of the melted material, triggered by this treatment and leading to the reduction of the heterogeneity of the chemical composition within the layer, seems to be correct.

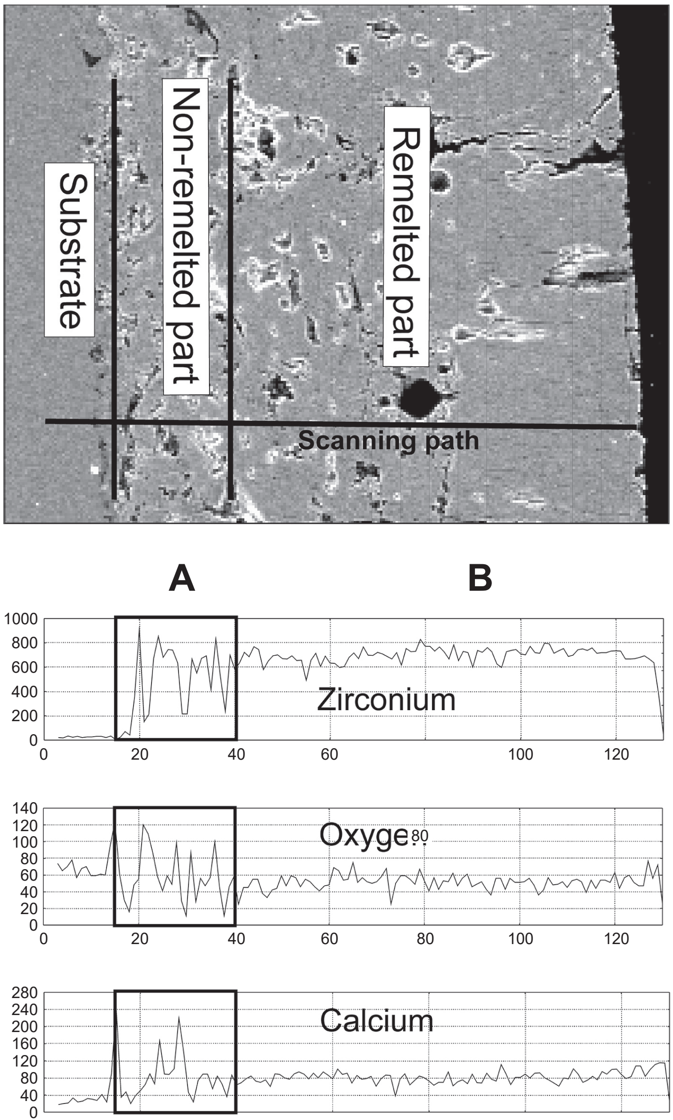

Fig. 5. The results of EDX analysis

4. Conclusions

In the course of the research, it was determined that:

1. The remelting treatment and the rapid crystallisation of the melted material, triggered by it, leads to a reduction of the heterogeneity of the chemical composition of the coating material and a loss of structural features typical for plasma-sprayed coatings, in particular the laminar nature of the structure and its porosity.
2. Application of the dual torch system, with the independent arc for remelting the surface layer of plasma-sprayed coatings, is a very promising solution which enables effective remelting of non-conductive oxide coatings.
3. The increase of the current intensity led to an increase in the depth of the remelted zone, but the risk of disadvantageous changes in the surface geometry was increased too. To a minor degree, the changes in the surface roughness were a function of the velocity of the heat source.
4. Remelting of the surface layer using the GTAW method may be an alternative solution to laser technologies, and due to its cost competitiveness, simplicity of operation and the availability of equipment, it seems to be a remarkably attractive tool.

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