**Archives of Materials Science and Engineering**

Volume 33
Issue 1
September 2008
Pages 39-44

International Scientific Journal
published monthly by the
World Academy of Materials
and Manufacturing Engineering

# Structural and phase investigations of oxide coatings of $TiO_2$ and $Al_2O_3$+13wt.%$TiO_2$ after remelting

A. Dudek*, J. Iwaszko
Institute of Materials Engineering, Czestochowa University of Technology,
Al. Armii Krajowej 19, 42-200 Częstochowa, Poland
* Corresponding author: E-mail address: dudek@mim.pcz.czest.pl

Received 06.05.2008; published in revised form 01.09.2008

## ABSTRACT

**Purpose:** The purpose of this work was a microstructural and phase analysis of oxide layers remelted with TIG welding machine and by means of modified TIG method.

**Design/methodology/approach:** The scope of investigations encompassed microstructural and phase assessment of oxide layers after remelting and alloying. Surface treatment was performed by means of TIG welding method and its modified version.

**Findings:** Investigations of remelted coatings enabled determination of effect of the treatment on the structure and nature of phase transformations.

**Research limitations/implications:** Further investigations with use of transmission electron microscopy will make it possible to observe the microstructures and obtain additional information about morphology of phases.

**Practical implications:** Oxide coatings are one of the main components in coatings which are used under conditions of intensive wear and influence of corrosion agents.

**Originality/value:** Modification of single-torch welding method was a solution to a problem of remelting of non-conducting ceramic coatings.

**Keywords: Welding; Surface treatment**

MATERIALS MANUFACTURING AND PROCESSING

## 1. Introduction

One of main components in coatings used under conditions of intensive wear and influence of corrosion and temperature agents include oxides. These compounds are characterized with exceptional combination of heat and mechanical properties, which makes them indispensable for a variety of applications. Process of oxide coatings formation is usually performed by means of APS, PVD (Physical Vapour Deposition), CVD (Chemical Vapour Deposition, or HVOF (High Velocity Oxy-Fuel) methods. Plasma spraying is also among the most popular methods. Easiness of use, popularity of technology and lower manufacturing costs constitute arguments in favour of plasma spraying. A factor which limits positive assessment of this method is a high level of porosity of coatings and low adhesion of the layer to base material. These features result both from the specific nature of plasma spraying and properties of used powders [1-11].

Thus, obtaining of layers with possibly lowest porosity and high adhesion to base material have become priorities in modern surface engineering [1-16]. This is possible e.g. through additional heat treatment leading to layer remodelling. Application of high-energy heat sources (laser, plasma, welding methods) and triggering of remelting effect in coatings seems to be a very interesting solution.

According to references laser techniques are more and more popular, which might be explained by possibility of precision focus of very large amount of energy on selected element of material and triggering of rapid crystallization. TIG welding method is also worth mentioning – its advantages include popularity of the technology, low cost of equipment, simplicity of use etc. This method was used for remelting of plasma – sprayed coating and steel alloying.

## 2. Description of the research

Materials used for investigations included oxide coatings of $TiO_2$ and $Al_2O_3$ + 13%wt.$TiO_2$ prepared by means of plasma spraying using PN 120 set. Thickness of the obtained coatings was varied and within the range from 20–200 μm, which resulted from the assumed investigative and utilization goals.

Coatings were made on cuboid surfaces of samples made of 40Cr4 steel ($TiO_2$ coatings) and X5CrNi18-10 steel ($Al_2O_3$+$TiO_2$ coatings).

Summary of coatings deposition parameters is presented in Table 1.

Table 1.
Summary of coating deposition parameters

| Plasma-spraying equipment used | PN-120, ZDAU-IBJ, Poland |
|---|---|
| Powder materials | $TiO_2$<br>$Al_2O_3$ + 13%wt.$TiO_2$ |
| Powder granulations | 50±20μm |
| Substrate coated | 40Cr4, X5CrNi18-10 |
| Voltage | 62-65 V |
| Current | 520A |
| Spraying distance | 130 mm |
| Cooling of substrate | Air blow |
| Coating thickness | 20 – 200 μm |

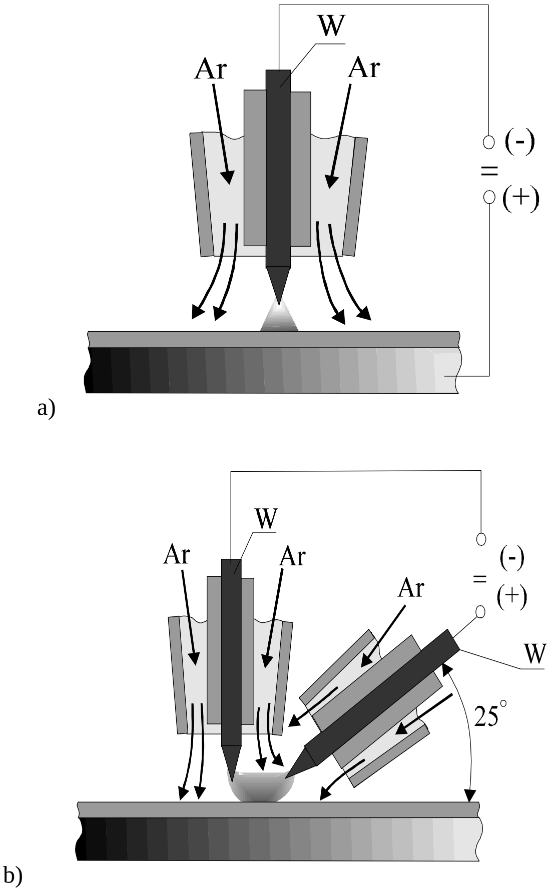
The investigated coatings were remelted by means of TIG welding machine ( $TiO_2$ coatings (Fig.1a)) and a modified TIG method ($TiO_2$ coatings and $Al_2O_3$+$TiO_2$) (Fig. 1b). Modification of TIG method was sparked by a necessity to find solution to a problem of lack of electrical conductivity in oxide materials. The effect of the undertaken activities was preparation of the method which enabled remelting of coating materials with varied compositions and thermo-physical properties, including non-conductive materials. The two-torch arrangement prepared for the purposes of the experiment enabled use of heat energy in arc without necessity of involving the coating in the process of manufacturing and stabilization. Graphical presentation of the applied arrangement is shown in Fig. 1b. Detailed information on methodology of remelting by means of the modified TIG method and the classical method were presented in previous papers [6-10].

Main investigation purpose of this work was assessment of oxide coatings obtained as a result of remelting by means of TIG welding method and its double-torch version.

Another investigation aspect considered within the work was an analysis of phase composition in the investigated coatings as a result of the treatment. Particularly interesting issue is characteristics of polymorphic transitions in $TiO_2$ as a function of coating composition and surface treatment conditions.

The scope of X-ray tests encompasses analysis of phase composition of the powder, sprayed coating and the coating after surface treatment.

In order to fulfil the assumptions and investigative purposes, oxide material was subject to metallographic investigations by means of Neophot 23 optical microscope and JEOL JSM 5400 scanning microscope. The investigations of phase composition was made by means of X-ray Seifert XRD-3003 diffractometer.



a)

b)

Fig. 1. Methodology of remelting of oxide coatings: TIG method (a) and modified TIG method (b)

## 3. Experimental results

The investigations revealed considerable changes in modified coatings for all the used materials and for both methods of treatment. These changes manifested in deterioration in porosity, better homogeneity and in case of higher current parameters – creation of the alloyed surface layers. As observed during investigations, mixing of coating material with base material took place and, consequently, change in chemical composition of surface layer in base material.

Microstructural investigations revealed presence of cellular and dendrite structures in the analysed layers (both remelted and alloyed ones) and locally also column structures (Figs. 2-6). Type of the created microstructure was a function of the applied treatment parameters.

Structural investigation also revealed presence of numerous microcracks. Their nature is presented in Figs. 7-9. Moreover, it was also observed that in the case of a modified TIG method the number of microcracks is by far lower. Appearance of microcracks was a consequence of very fast rates of heating and cooling accompanying surface treatment. Uneven outflow of heat from remelted mass and low thermal conductivity of oxides had also impact on local loss in compactness of the material.

The investigations of surface layers obtained after treatment with TIG method and its modified version revealed distinct rise in current-voltage parameters on geometrical structure of the band. Macroscopic view of paths obtained for the tested samples revealed intensive unevenness and large cavities.

In the case of samples subject to alloying, a characteristic feature was presence of an outflow on the edge of the band. Creation of the outflow was caused by moving of the melted material as a result of dynamic influence of shielding gases. Ultra-short times of heating and cooling of material accompanying surface treatment increased tendency to appearance of outflows. As it was observed during microstructural investigations, a needle-based structure was mainly formed in outflows (Figs. 10-11).

Another investigation stage incorporated an analysis of phase composition of powder, sprayed coatings and layers after surface treatment. The obtained diffractograms of powder and $TiO_2$ are presented in Figs. 12-14, while $Al_2O_3$ + $TiO_2$ in Figs. 15-17.

Investigations of phase composition of $TiO_2$ powder revealed presence of three polymorphous modifications of titan oxide: brookite with orthorhombic cell, rutile and anatase with tetragonal cell (Fig. 12).

In both sprayed and alloyed surface layer a presence of rutile was revealed, which is confirmed by the fact of polymorphous transition in remaining two modifications of $TiO_2$ (Figs. 13, 14).

Moreover, the alloyed surface layer revealed presence of the phase coming from base material i.e. Feα phase, which proves alloying process.

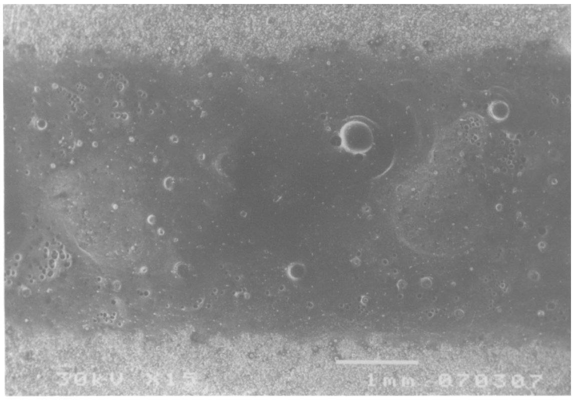


Fig. 2. Remelted oxide coating $TiO_2$ (TIG welding machine)

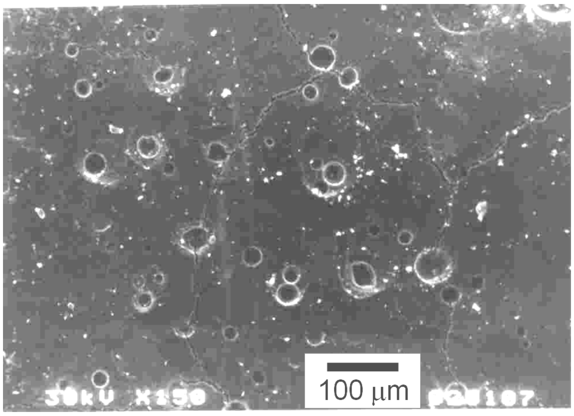


Fig. 3. Remelted oxide coating $Al_2O_3$ + $TiO_2$ (TIG welding machine)

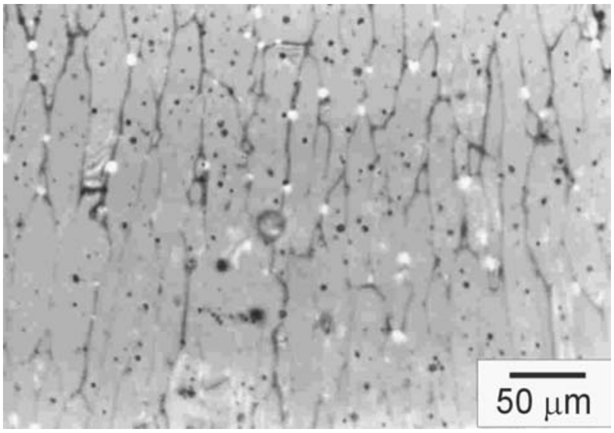


Fig. 4. Structure of remelted oxide coating $Al_2O_{3+}TiO_2$ (TIG welding machine)

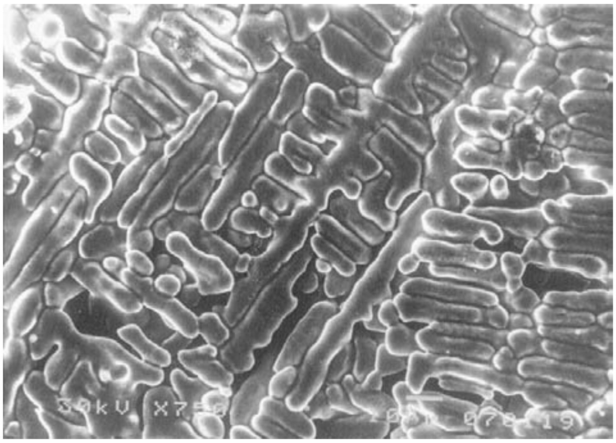


Fig. 5. Structure of remelted oxide coating $TiO_2$ by a set of torches

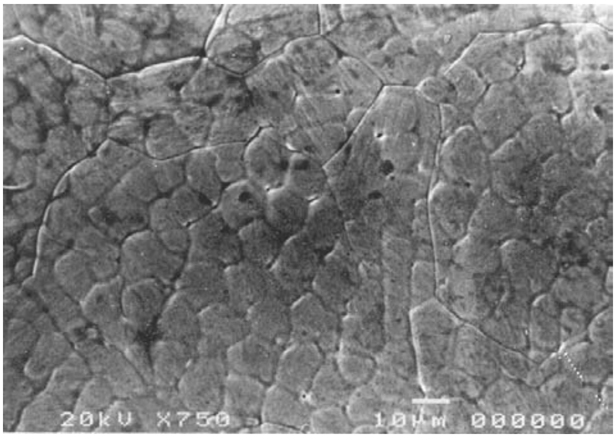


Fig. 6. Structure of remelted oxide coating $TiO_2$ (TIG welding machine)

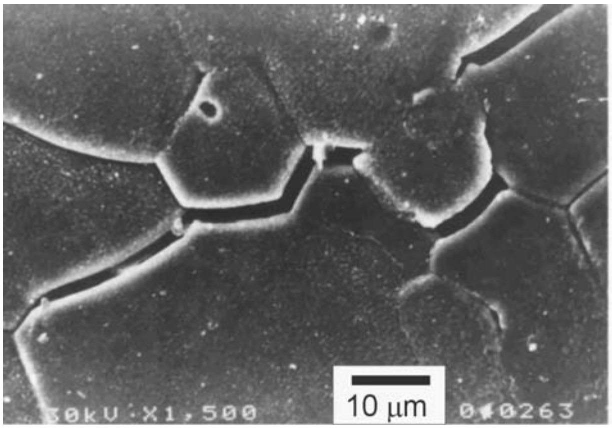


Fig. 7. Structure of remelted oxide coating $Al_2O_{3+}TiO_2$ (TIG welding machine)

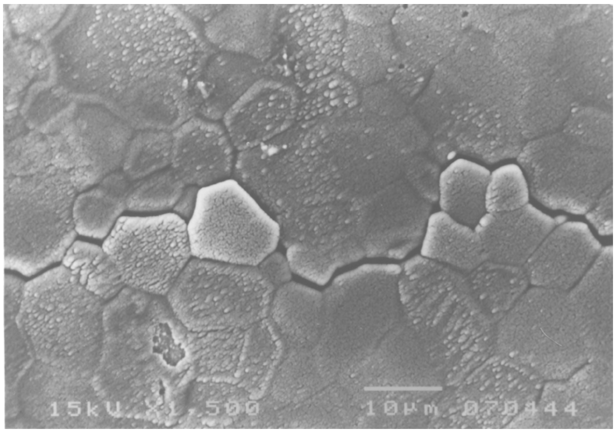


Fig. 8. Structure of remelted oxide coating $TiO_2$ (TIG welding machine)

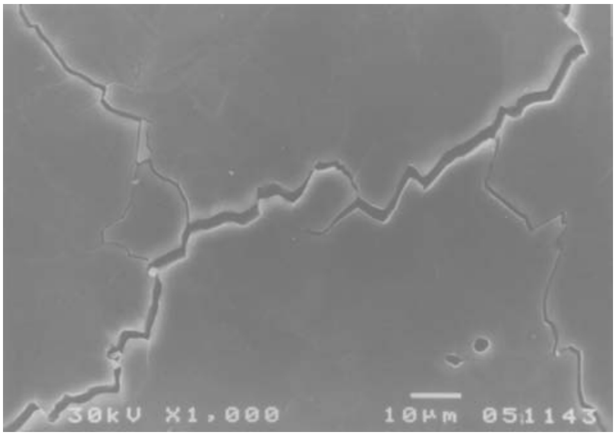


Fig. 9. Structure of remelted oxide coating $TiO_2$ with a set of torches TIG

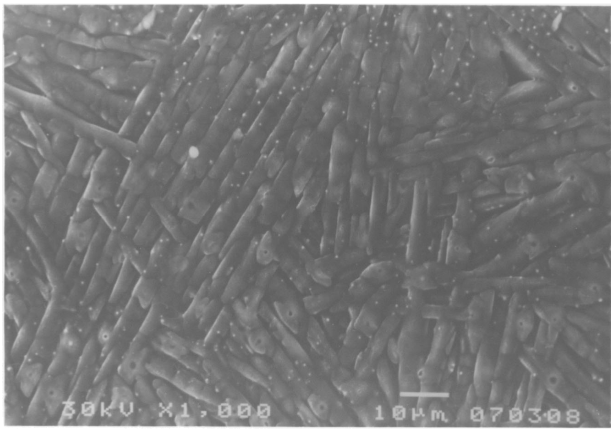


Fig. 10. Structure of the outflow created from remelting of $TiO_2$ oxide coating (TIG welding machine)

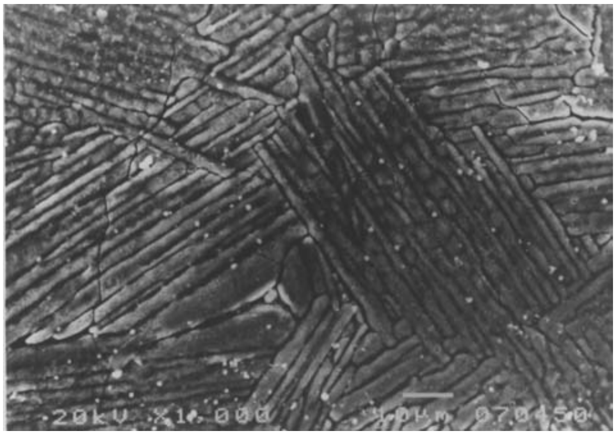


Fig. 11. Structure of the outflow created from remelting of $TiO_2$ oxide coating by a set of torches

Far more complex transitions took place in $Al_2O_3$ + $TiO_2$, which seems to be obvious in consideration of polimorphic complexity of $Al_2O_3$, as this compound appears in a few polymorphous modifications, the most important including: [ 9-11] thermodynamically stable modification of $\alpha$-$Al_2O_3$ with hexagonal lattice densely packed and metastable modification of $\gamma$-$Al_2O_3$ with face-centred regular lattice. There are also tetragonal, hexagonal, orthorhombic and monoclinic modifications.

Phase composition investigations (Fig. 15) revealed presence of two phases, namely hexagonal $\alpha$-$Al_2O_3$ and tetragonal $TiO_2$ (rutile) ones.

X-ray analysis of sprayed coatings (Fig. 16) revealed presence of both main polymorphic modifications of $Al_2O_3$, i.e. both $\alpha$ and $\gamma$. A dominating phase in this case was $\gamma$–$Al_2O_3$ modification. Reflexes from thermodynamically stable $\alpha$–$Al_2O_3$ modification (prevalent in the powder) were distinctly weaker. Presence of $\alpha$–$Al_2O_3$ form in the sprayed layer can be explained by uncompleted remelting of particles during its spread on base material.

Fast crystallization, however, is responsible for constitution of phase composition in the sprayed coatings, characterized by domination of non-equilibrium phases and structures.

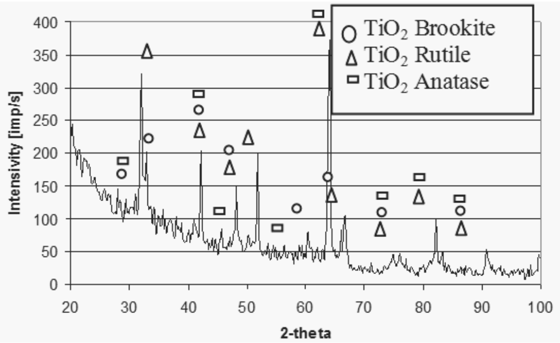


Fig. 12. Example of diffractogram of $TiO_2$ powder

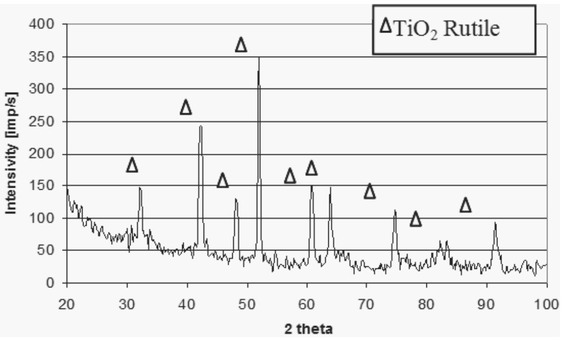


Fig. 13. Example of diffractogram of $TiO_2$ coatings

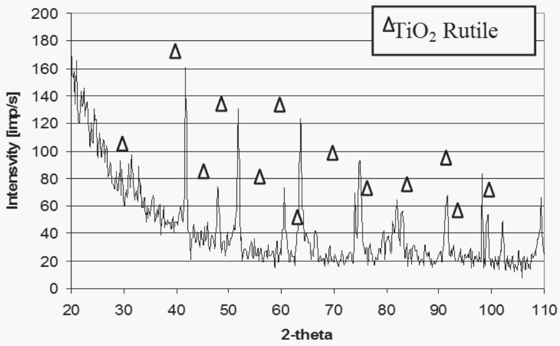


Fig. 14. Example of diffractogram of remelted $TiO_2$ coatings

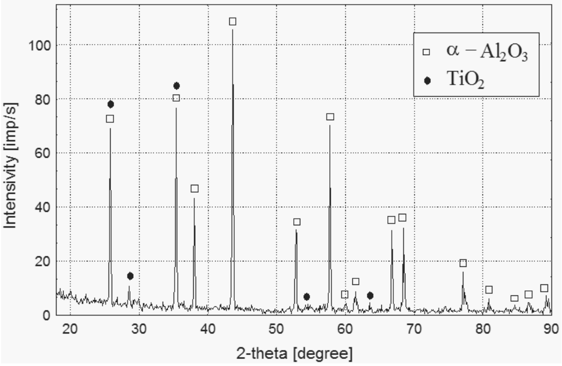


Fig. 15. Example of diffractogram $Al_2O_3$ + $TiO_2$ powder

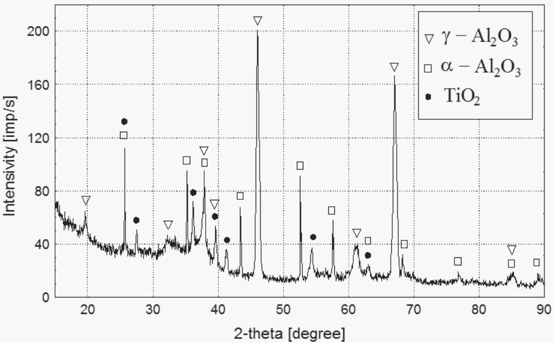


Fig. 16. Example of diffractogram of $Al_2O_3$ + $TiO_2$ coatings

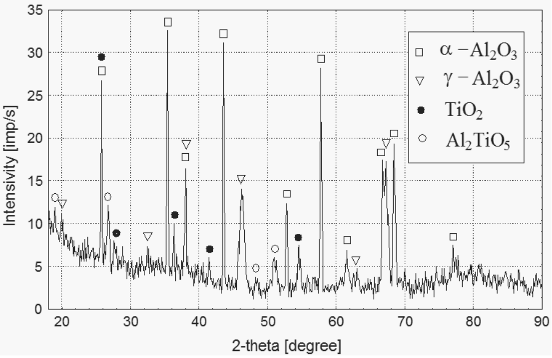


Fig. 17. Example of diffractogram of remelted $Al_2O_3$ + $TiO_2$ coatings

One should also consider here thermodynamic aspects of the process and the resulting principle which says that each arrangement tends to reach a state with corresponding possibly lowest level of free energy, regardless of the fact if this state will be connected with creation of a metastable or thermodynamically stable modification.

In order to understand the role of $TiO_2$ in composition with $Al_2O_3$, as well as in order to verify the thesis of impact of $TiO_2$ on quantity relations which are formed between $\alpha$ and $\gamma$ modifications, a phase analysis of $Al_2O_3$ without addition of $TiO_2$ was carried out. Pure powder of $\alpha-Al_2O_3$ was used to produce the coating.

The investigations revealed presence of both polymorphous forms of $Al_2O_3$, however, contribution of metastable modification of $\gamma-Al_2O_3$ was higher than for the one registered in analogues coatings containing addition of $TiO_2$. Stabilizing role of $TiO_2$ in oxide compositions based on $Al_2O_3$ was therefore proved.

Remelting of the coating, as can be observed in Fig. 17, triggered phase transition of $\gamma\rightarrow\alpha$, whose consequence was rise in contribution of $\alpha-Al_2O_3$ phase at the expense of metastable form of $\gamma-Al_2O_3$ prevalent in the sprayed material.

Analysis of phase composition in the coatings, as a function of the applied remelting methods and the accepted parameters of treatment enabled observation of a few significant regularities. It has been observed that the increase of linear energy of electric arc results, in most of cases, in intensification of $\gamma\rightarrow\alpha$ transition, whose consequence was increase in $\alpha$ modification contribution. Another feature characteristic of phase composition in remelted material, as compared to sprayed coating or output powder, was presence of orthorhombic aluminium titanate ($\beta$-$Al_2TiO_5$) and tetragonal $TiO_2$. Existence of both phases at the same time proves that only a part of $TiO_2$.reacted with $Al_2O_3$ during remelting while the rest maintained its primary form and nature.

This state should be explained by specific conditions which appear during layer treatment. High temperature gradient as well as very short time of coating material solidification undoubtedly reduced possibility of total $TiO_2$ reaction and they prevent from phase transition of $\beta$-$Al_2TiO_5$.

In consideration of the fact that during processes of friction and wear not only places of real interface of elements on their surfaces are involved, but also a particular volume of material in surface zones, it is obvious that conscious formation of surface layer state in order to obtain the most favourable distribution of residual stress. This distribution is supposed to prevent unfavourable phenomena which occur in utilized surface layer. It is commonly known that considerable residual compressive stress which occurs in hardened surface layers results in considerable increase in fatigue resistance of machine and tool parts throughout the whole volume, but also cyclic contact/impact/heat load. Main source of residual stress in graphically presented in Fig. 18.

Due to the abovementioned facts, the obtained modified surface layers were subject to residual stress tests. Stresses were determined by the X-ray diffraction (XRD) method. Investigations of residual stress carried out in remelted coatings for both methods revealed presence of tensile stress at the level of - 150 MPa to - 250 MPa (for TIG remelting and for the coatings remelted by means of double-torch TIG arrangement).

Presence of tensile state of residual stress in surface layers should be explained by the changes in density, porosity or rigidity of the remelted coatings.

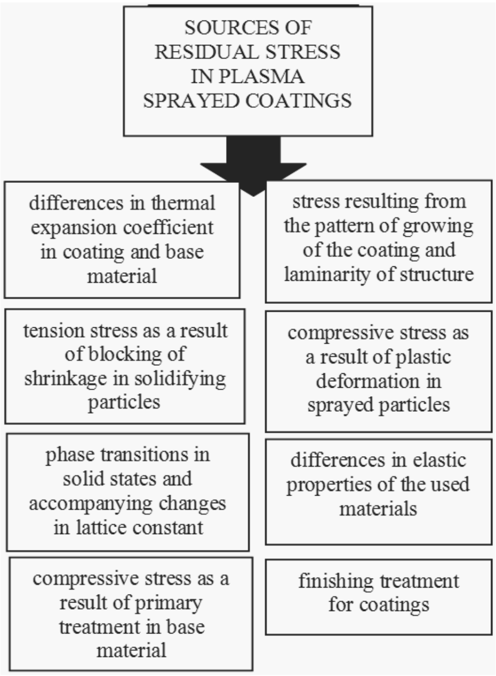


Fig. 18. Main sources of residual stress in plasma-sprayed coatings

## 4. Conclusions

Use of high-energy sources of heat brings opportunities to obtain remelting effect in oxide coatings and with higher current/voltage parameters also opportunities of alloying of surface layer in steel base material.

Application of modified TIG method enables limitation of outflows during the process of steel alloying.

In conditions of spraying and surface treatment polymorphous transitions of $TiO_2$ and $Al_2O_3$ take place, and in case of $Al_2O_3$ +$TiO_2$ coatings also reaction leading to appearance of aluminium titanate.

Presence and amount of microcracks are the resultant of the accepted current-voltage parameters, and the applied remelting variant in particular.

Presence of tensile state of residual stress in surface layers should be explained by the changes in density, porosity or rigidity of the remelted coatings.

The remelting treatment of the coatings can be carries out by means of the modified TIG welding technology, employing the independent arc principle, without direct engagement of the coating for the initiation and maintenance of the electric arc.

## References

[1] A. Dudek, Z. Nitkiewicz, H. Stokłosa, Analysis of the arc shape during remelting process, Materials Science 5 (2005) 34-37 (in Polish).

[2] T. Burakowski, T. Wierzchoń, Metals surface engineering. WNT, Warsaw, 1995 (in Polish).

[3] A. Dudek, Z. Nitkiewicz, The structure properties of surface layers which were obtained by alloying process, Acta Metallurgia Slovaca 8 (2002) 339-343.

[4] A. Dudek, Z. Nitkiewicz, Diagnostics of plasma arc during the process of remelting of surface layer in 40Cr4 steel. Archives of Materials Science and Engineering 28/6 (2007) 369-372.

[5] J. Iwaszko, Surface and Coatings Technology 201/6 (2006) 3443.

[6] J. Iwaszko, K. Kudła, Z. Nitkiewicz, R. Kruzel, Application of welding technologies in remelting for plasma sprayed coatings, Welding Rewiev 12 (2004) 7-12.

[7] J. Iwaszko, Z. Nitkiewicz, K. Sławuta, I. Przerada, Remelting treatment of plasma sprayed coatings, Materials Engineering 3/140 (2004) 597-600.

[8] J. Iwaszko, Z. Nitkiewicz, Application of remelting surface treatment for the process of formation of structure and properties of oxide coatings of $Al_2O_3$+13%$TiO_2$, Materials Engineering 3/151 (2006) 399-402.

[9] M. Uma Devi, New phase formation in $Al_2O_3$-based thermal spray coatings, Ceramics International 30/4 (2004) 555-565.

[10] Tevo.net:baza wiedzy, http://www.tevo.net/w_bazaw.

[11] M. Uma Devi, On the nature of phases in $Al_2O_3$ and $Al_2O_3$–SiC thermal spray coatings, Ceramics International 4 (2004) 545-553.

[12] L.A. Dobrzański, Fundamental of materialsand metal science, WNT, Warsaw, 2002 (in Polish).

[13] A. Grabowski, B. Formanek, M. Sozańska, M. Nowak, Laser remelting of Al.-Fe-$TiO_3$ composite powder incorporated in a aluminium matrix, Journal of Achievements in Materials and Manufacturing Engineering 18 (2006) 95-98.

[14] W. Serbiński, B. Majkowska, Microstructure and corrosion properties of the laser treated superston alloy, Journal of Achievements in Materials and Manufacturing Engineering 18 (2006) 415-418.

[15] A. Zieliński, M. Jażdzewska, A. Narożniak, W Serwiński, Surface structure and properties of Ti6Al4V alloy laser melted at cryogenic conditions, Journal of Achievements in Materials and Manufacturing Engineering 18 (2006) 423-426.

[16] L.A. Dobrzański, E. Jonda, A. Polok, Effect of laser treatment on changes of the surface layers properties of the hot work alloy tool steels, Proceedings of the 13th Scientific International Conference „Achievements in Mechanical and Materials Engineering" AMME'2005, Gliwice–Wisła, 2005, 137-142.