DE GRUYTER OPEN
ADVANCES IN MANUFACTURING SCIENCE AND TECHNOLOGY
Vol. 41, No. 2, 2017
DOI: 10.2478/amst-2017-0012

THE INFLUENCE OF PLASMA GASES COMPOSITION AND POWDER FEED RATE ON MICROSTRUCTURE OF CERAMIC COATINGS OBTAINED BY PLASMA SPRAY PHYSICAL VAPOUR DEPOSITION (PS-PVD)

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Summary

The article presents results of research on the influence of the chemical composition of the plasma plume and the powder feed rate on microstructure and thickness of the ceramic coating deposited on IN617 alloy substrate by Plasma Spray Physical Vapour Deposition (PS-PVD) method. There were used three powder feed rates: 2, 10 and 30 g/min and five different compositions of plasma gas (Ar, He, H_2 and O_2). Current – 2200 A, a sample rotation speed – 20 RPM and pressure inside of chamber – 150 Pa was fixed. The results showed that it is possible to deposit ceramic layer with lamellar and columnar structure, depends on process parameters. Columnar structure, characteristic for the PS-PVD process, is possible to obtain when the energy of plasma plume is sufficient for evaporating ceramic powder and deposit in on the substrate. The columnar-like structure coatings were obtained in the process with the highest amount of He – 60 dm^3/min and lower values of powder feed rate – 2 and 10 g/min. Such effect was observed independently from the additional flow of H_2 and O_2. The columnar-like structure was possible to deposit also with 30 g/min feed rate. However, evaporation of ceramic powder occurred only in the process with only Ar and He in mixture – respectively 35 and 60 dm^3/min and with addition only 2 dm^3/min O_2 to it. Nevertheless, inside the structure a lot of unmelted particles was visible.

Keywords: Low Pressure Plasma Spray, LPPS, PS-PVD, Plasma Spray Physical Vapour Deposition

Wpływ składu chemicznego gazów plazmotwórczych oraz natężenia przepływu proszku na mikrostrukturę warstwy ceramicznej powłokowej bariery cieplnej wytworzonej w procesie fizycznego osadzania z fazy gazowej z odparowaniem w strumieniu plazmy

Streszczenie

W pracy ustalono wpływ składu chemicznego mieszaniny gazów plazmotwórczych i natężenia przepływu proszku na budowę warstwy ceramicznej na podłożu nadstopu niklu IN-617. Warstwy wytworzono w procesie fizycznego osadzania z fazy gazowej z odparowaniem za pomocą palnika plazmowego (Plasma Spray Physical Vapour Deposition – PS-PVD). Przyjęto natężenie przepływu proszku: 2, 10 i 30 g/min oraz różny skład chemiczny mieszaniny gazów plazmotwórczych (Ar, He, H_2 i O_2). Stosowano natężenie prądu palnika – 2200 A, prędkość obrotową stołu – 20 obr/min oraz ciśnienie w komorze roboczej – 150 Pa. Analiza wyników badań pozwoliła ustalić, że proces fizycznego osadzania z fazy gazowej z odparowaniem w strumieniu plazmy umożliwia wytworzenie warstwy ceramicznej o budowie lamelarnej i kolumnowej. Budowę kolumnową warstwy, charakterystyczną dla procesu PS-PVD, uzyskano dla energii strumienia plazmy zapewniającej odparowanie podawanego proszku. Warstwy takie wytworzono przy dużym natężeniu przepływu He – 60 dm^3/min i małej wartości natężenia przepływu proszku – 2 i 10 g/min. Efekt ten był obserwowano niezależnie od natężenia przepływu H_2 oraz O_2. Budowa kolumnowa warstwy możliwa jest również do

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wytworzenia przy największym natężeniu przepływu proszku – 30 g/min. Odparowanie i osadzenie warstwy ceramicznej stwierdzono tylko dla mieszaniny Ar + He o natężeniu przepływu – odpowiednio 35 i 60 dm^3/min oraz dla mieszaniny Ar + He z dodatkowym wprowadzenie tlenu O_2 o natężeniu przepływu – 2 dm^3/min. Wytworzone warstwy cechowały się wówczas występowaniem nieodparowanych cząstek proszku.

Słowa kluczowe: natryskiwanie plazmowe w warunkach obniżonego ciśnienia, fizyczne osadzanie z fazy gazowej z odparowaniem w strumieniu plazmy, PS-PVD

1. Introduction

Different plasma spraying technologies have been developing for over 40 years. Development of Air Plasma Spraying (APS) in case of oxidation of molten particle results in Low Pressure Plasma Spraying (LPPS) method. However, in LPPS method it is impossible to obtained thin homogenous coating like in Physical or Chemical Vapour Deposition (PVD or CVD) method. Recently, hybrid technologies were developed in order to combine advantages of thermal spraying and PVD/CVD processes. The source of plasma in hybrid methods is a high power plasma torch. The coating material is vaporised, similarly to the PVD/CVD methods and accelerated towards substrate like a molten droplet in LPPS. There are three different hybrid technologies:

- *Low Pressure Plasma Spraying – Thin Film* – LPPS-Thin Film,
- *Plasma Spray – Physical Vapour Deposition* – PS-PVD,
- *Plasma Spray – Chemical Vapour Deposition* – PS-CVD [1].

The PS-PVD method is an alternative for very expensive Electron Beam-Physical Vapour Deposition (EB-PVD) method [2, 3]. The first usage of this method was to deposit ceramic layer in the thermal barrier coating, which has a column-like structure similar to that, produced by EB-PVD [4, 5]. The main difference between this two methods is deposition rate – which is much faster in PS-PVD. Moreover, PS-PVD is non-line of sight process which is a drawback of the EB-PVD method.

First data on the influence of process parameters used in the PS-PVD method on the microstructure of the formed ceramic layer was studied in the paper of B. Harder, D. Zhu [6]. Experimental studies were conducted at a variable plasma gun output value (1600-1800), the plasma gas flow rates (80, 100 and 120 dm^3/min) and participation of Ar and He in the total flow in the following ratio 2: 1/1: 1/1: 2. It has been demonstrated that an increase in the flow rate of helium and in the total flow of plasma gases have caused an increase in energy of the plasma jet and the voltage measured at the gun. Analysis of the microstructure has shown that a decrease in the pressure in the chamber and an increase in the energy of the plasma current allow forming a coating of the column-like structure. Higher pressure in the chamber and smaller energy of the plasma jet result in forming a thick dense coating. This also results in the presence of two allotropic forms of zirconium oxide in the coating – tetragonal and monoclinic (for flow values of 80 dm^3/min Ar and 40 dm^3/min He, a pressure of 200 Pa, a current of 1400A).

The influence of the chemical composition of the plasma gas and feed power were examined by Mauer et al. [7]. On the basis of tests on spectroscopic plasma plume with different chemical composition it has been shown that the highest enthalpy) of 838.965 J/mol at a constant electric power of the gun and the pressure in the working chamber can be obtained for a plume with a flow rate of He = = 60 dm^3/min and Ar = 35 dm^3/min. Additional hydrogen flow to the plasma plume at the rate of 10 dm^3/min causes a decrease in enthalpy by 768.41 J/mol and resulted in increasing the amount of melted and unvaporized particles.

The authors explained this occurrence as caused by the lower enthalpy of the plasma plume (733.496 J/mol). A second reason for the low level of evaporation was a separation of gas components in the cross-section of the plasma plume. Spectroscopic analysis has shown that helium accumulates in the centre of the plasma plume, while the remaining components remain outside. Introducing hydrogen causes the concentration of argon plasma along the jet axis. The authors have found that the increase in the powder feed of > 20 g/min results in an insufficient degree of evaporation of the powder particles.

Studies by Hospach et al. [8] show the impact exerted by the kinematics of motion of the gun and the substrate on the microstructure of the YSZ coating. A low rotational speed of the sample allows for construction of corrugated coating, also referred to as a „zig-zag", characterised by lower thermal conductivity. Increasing the inclination angle in the pendulum movement of the plasma torch resulted in lowering the temperature of the substrate, and thus formation of a coating containing multiple layers composed of columnar grains.

In present studies, the influence of different chemical composition of plasma gases, especially additional gases like hydrogen, oxygen as well as powder feed rate, on structure of coatings was described

2. Experimental

The research plan was developed based on previous experimental trials for producing thermal barrier coatings in the Research & Development Laboratory for Aerospace Materials at RUT [9, 10] and recent publications on the effect of the PS-PVD process on the properties and microstructure of the ceramic layer [4, 6-12]. The tests were subject to the following process parameters of spraying:

- the chemical composition of the plasma gas – there were introduced four plasma-forming gases: argon, helium and hydrogen and oxygen,
- the feed rate of powder – in the present study an attempt was made to increase the flow of powder to high values, not tested in any of the research centres involved in the PS-PVD process, and to reduce it to a small flow.

The heat-resistant Inconel 617 type nickel superalloy was chosen as a substrate material. Chemical composition is shown in Table 1.

Table 1. Chemical composition of Inconel 617 alloy

Content, % mas.													
Ni	**Co**	**Cr**	**Mo**	**Al**	**Ti**	**Zr**	**C**	**Fe**	**Mn**	**Si**	**S**	**Cu**	**B**
Base	12	22	9	1	0.6	0.06	0.1	3	1	1	0.015	0.6	0.006

The bond coat was a diffusion aluminide coating (NiAl) produced by chemical vapour deposition (CVD). The process was conducted using a BPX Pro 325S system by Ion Bond. Parameters for the low-activity aluminide coating were as follows: duration 12 h, temperature 1040^{o}C, the flow of hydrogen chloride: 0.2 dm^3/min, of hydrogen 10.5 dm^3/min. Before applying the ceramic coating the samples were not sanded but only cleaned in isopropanol.

The standard PS-PVD process parameters applied in the test were as follows: pressure – 150 Pa, power current – 2200A, sample rotation speed – 20 RPM, plasma gas flow Ar – 35 dm^3/min, He – 60 dm^3/min, powder feed rate – 10 g/min. Zirconia oxide powder stabilised by yttria oxide, Metco 6700 type (Oerlikon-Metco) was used in the tests. Values of the investigated parameters were determined in accordance with the values shown in Table 2.

Table 2. Values of plasma-forming gas flows used in the tests

No of the gas composition	**Gas flow, dm^3/min**			
	Ar	**He**	**H_2**	**O_2**
C1	85	10	-	-
C2	35	60	-	-
C3	35	60	2	-
C4	35	60	2	2
C5	35	60	-	2

Variation in the amount of plasma gases and powder feed rate was carried out in accordance with the following scheme: for each of the five different configurations of the plasma gas flows shown in Table 2, there were carried out three processes at the powder feed rate of 2, 10 and 30 g/min respectively.

3. Results

The research has shown a strong influence of the chemical composition of the plasma gases and powder feed rate on the thickness of the ceramic coating (Fig. 1).

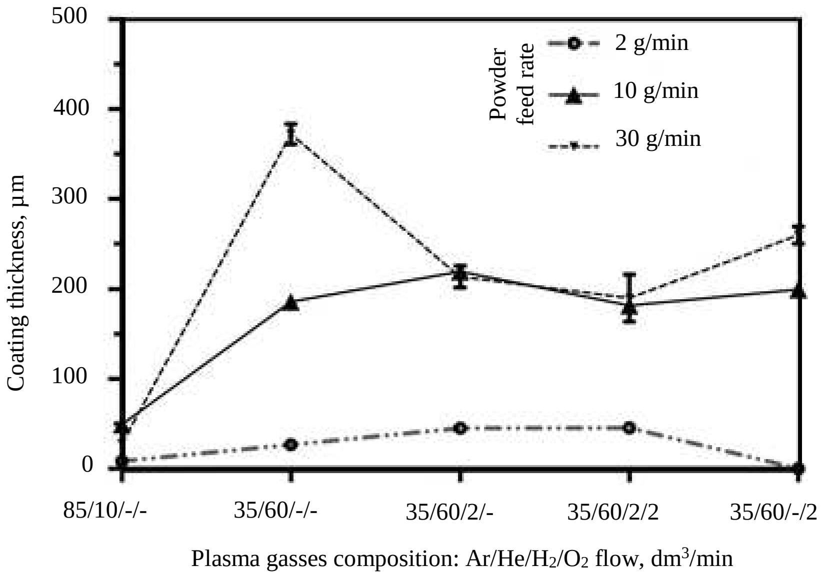

Fig. 1. The thickness of ceramic coating deposited by PS-PVD method using different plasma gases composition and powder feed rate

Plasma plume with a high flow rate of Ar = 85 dm^3/min and low flow rate of He = 10 dm^3/min (the composition designated C1 in Table 2) resulted in very thin ceramic coatings – regardless of the powder feed rate. Even at 30 g/min, a coating had a thickness of less than 40 µm. The coating was characterised by dense splat-like structure (Fig. 2a, c, e). According to the research by Hospach et al. [8], this effect was related to decreased plasma enthalpy despite the constant current at the plasma gun (2200 A).

The chemical composition of the plasma gases designated as C2 (Ar/He = = 35/60 dm^3/min) was set as a standard for the production of ceramic coatings by the PS-PVD method. Coatings obtained from this composition had greater thickness compared to the previous set of parameters – C1 (Fig. 1). Changing the powder feed rate from 2 to 10 g/min resulted in a nearly sevenfold increase in the coating thickness (from 26.86 up to 185.90 µm) and the change from 2 to 30 g/min almost 14-fold (up to 372.31 µm). The ceramic coating had a columnar structure for all values of the feed rate – 2, 10 and 30 g/min (Fig. 2b, d, f). Nevertheless, at the highest powder feed rate, numerous unvaporized particles were observed.

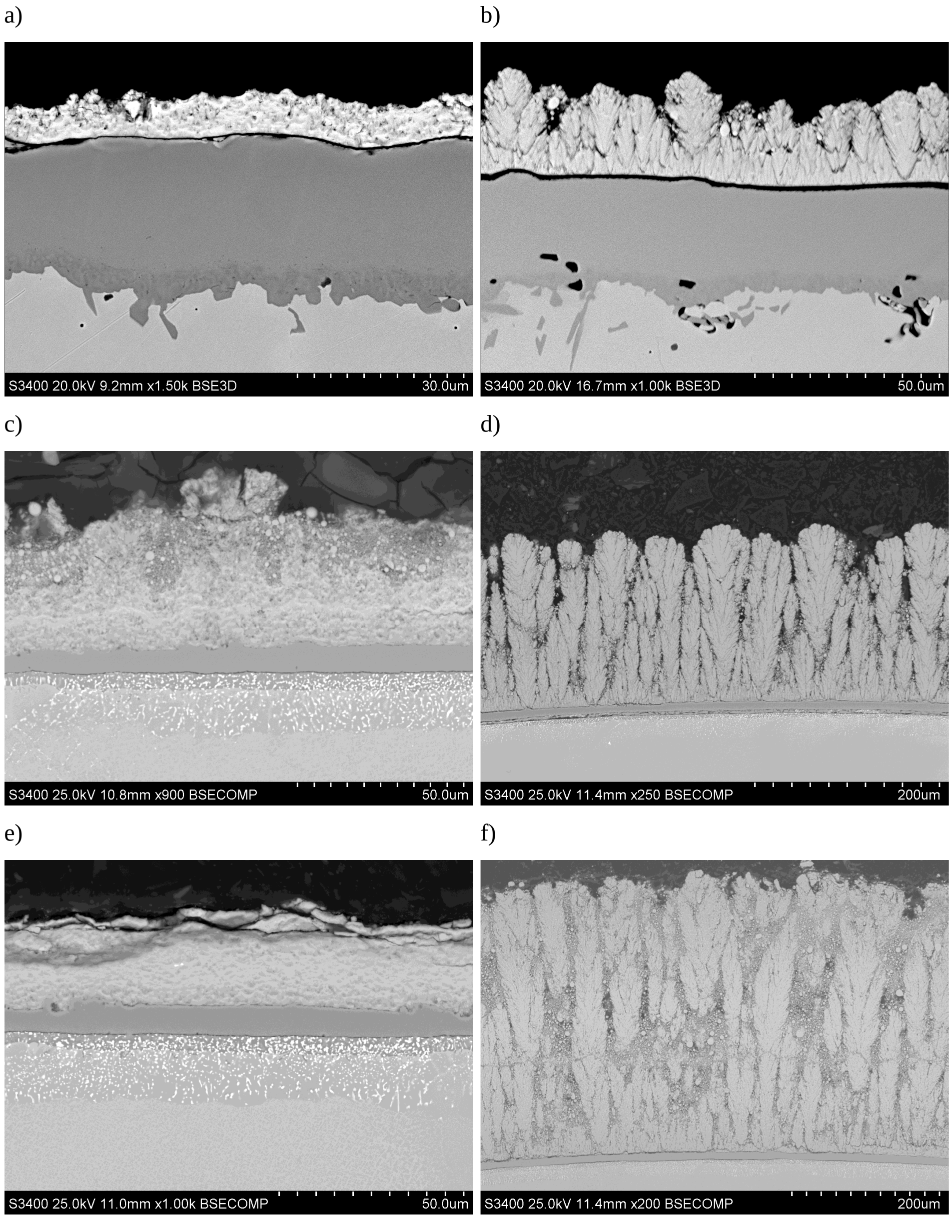

Fig. 2. The ceramic coating deposited for the chemical composition of plasma gases C1: Ar/He = 85/10 dm^3/min at the powder feed rate: a) 2 g/min c) 10 g/min e) 30 g/min and for the chemical composition of plasma gases C2 Ar/He 35/60 dm3/min at the powder feed rate: b) 2 g/min d) 10 g/min f) 30 g/min

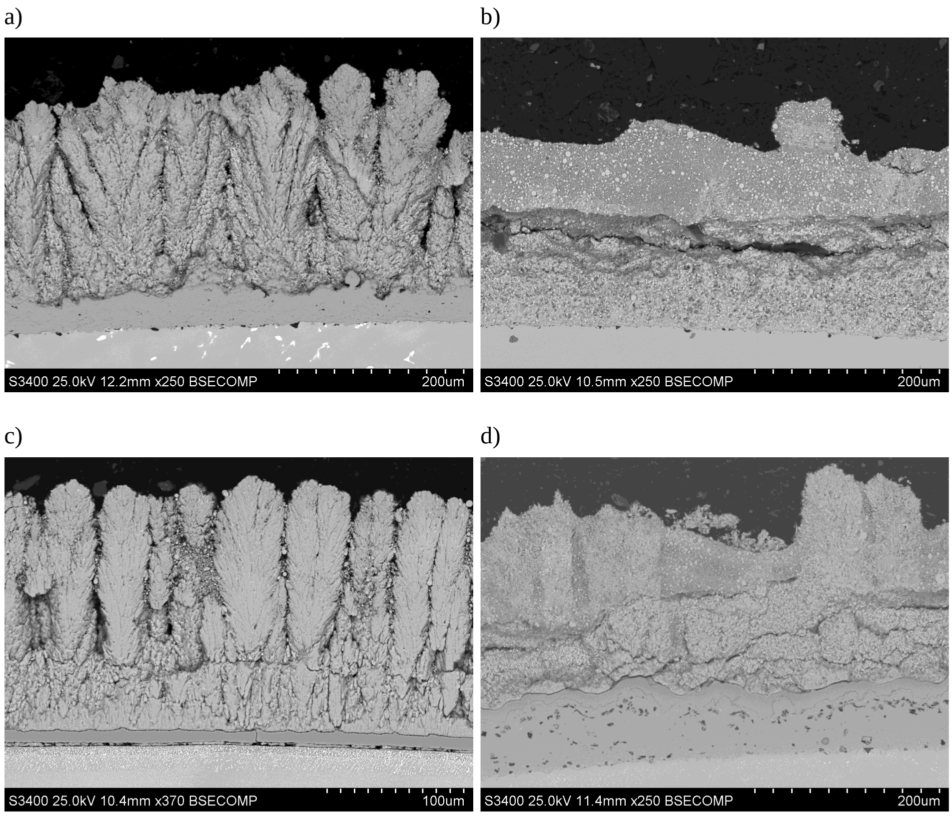

Fig. 3. The ceramic coating deposited for the chemical composition of plasma gases C3 Ar/He/H_2 35/60/2 dm^3/min at the powder feed rate: a) 10 g/min c) 30 g/min and for the chemical composition of plasma gases C4 Ar/He/H_2/O_2 35/60/2/2 dm^3/min at the powder feed rate: c) 10 g/min, d) 30 g/min

Additional hydrogen flow to the plasma plume at the rate of 2 dm^3/min with the standard flow rate of argon and helium (composition designated as C3: Ar/He/H_2: 35/60/2 dm^3/min) resulted in obtaining a coating of dark grey colour. This effect was associated with distortion of the structure of zirconium oxide – a smaller amount of oxygen atoms. There was observed the formation of columnar microstructure for the powder fed at 2 and 10 g/min (Fig. 3a). For the highest value of the powder feeding – 30 g/min – the coating had the splat-like structure (Fig. 3b). It was due to the lower enthalpy of the plasma plume with the addition of hydrogen compared to a standard mixture of Ar/He. The coating thickness was lower than those obtained with the standard parameters for 30 g/min – it was 214.12 μm and on a similar level for the rest of powder feed rate – 45.26 μm for the feed rate of 2 g/min and 219.9 μm for 10 g / min.

Simultaneous addition of oxygen and hydrogen to the plasma plume with standard composition (composition marked C4 $Ar/He/H_2/O_2$: 35/60/2/2 dm^3/min) have resulted in obtaining a coating with more clearly visible columns (for powder fed at 2 and 10 g/min – Fig. 3c). Similarly to the composition of $Ar/He/H_2$ 36/60/2 dm^3/min (gas composition marked C3), a larger amount of powder feed rate (30 g/min), results in dense ceramic layer characterised by a lack of columns – no evaporation occurred (Fig. 3d). The thickness of the obtained coatings was at a similar level to those described above

a) b)

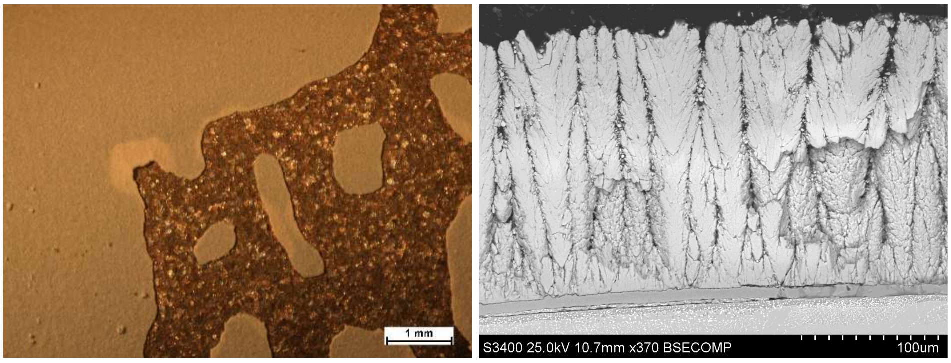

Fig. 4. The ceramic coating deposited for the chemical composition of plasma-forming gases C5 $Ar/He/O_2$ 35/60/2 dm^3/min at the powder feed rate a) 2 g/min (a stereoscopic microscopy image of the external surface), b) 10 g/min (SEM image of the microstructure)

In In the last series of tests to the standard chemical composition of plasma gases it was additional oxygen flow – composition C5 ($Ar/He/O_2$ 35/60/2 dm^3/min). The deposition process for such composition with a small amount of the powder feed rate (2 g/min) results in the flaking or falling off of the ceramic coating immediately after deposition (Fig. 4a). In the other two processes, deposited ceramic coating had the columnar structure (Fig. 4b). Additional oxygen flow to the plasma plume the standard Ar/He mixture of plasma gases did not result in lowering the temperature of the plasma plume, which would make it impossible to obtain a columnar microstructure. Coatings were characterised by the columnar structure. These results show that, even if the powder feed rate is at a high level (30 g/min), evaporation and deposition on the substrate still occurred. The thickness of the obtained coating was – 199.92 μm for the feed rate of 10 g/min and 259.79 μm for the powder fed at 30 g/min.

4. Summary

Presented results showed that changes in the chemical composition of the plasma gases and the powder feed rate had a strong influence on the microstructure of the ceramic coating used in TBC. PS-PVD deposition method enables to obtain both lamellar and columnar structure depending on process parameters.

A large amount of argon flow in the plasma plume (85 dm^3/min) resulted in – as desired – formation of coatings of minimum thickness for all the powder feed rates (2, 10 to 30 g/min). These coatings were characterised by splat-like structure, which was due to the low enthalpy of the plasma that does not allow for evaporation of the ceramic powder. These results were consistent with those carried out in Jülich [4, 5]. In previous research [6] it was demonstrated that the introduction of 60 dm^3/min of argon and 35 dm^3/min of helium allows obtaining a deformed columnar coating.

The greatest thickness of the ceramic coating was achieved for the values considered as standard deposition values, marked C2 (Power current 2200A, plasma gases Ar / He 35/60 dm^3/min, pressure: 150 Pa, samples rotation speed: 20 dm^3/min, powder feed rate of 30 g/min.) For all values of powder feed rate, for parameters marked C2 there was formed a coating of the columnar structure. Additional 2 dm^3/min H_2 flow to the plasma-forming gas mixture (parameters C3), as well as additional 2 dm3/min flow of hydrogen and oxygen at the same time (parameters C4), resulted in a reduction of the thickness of the ceramic coating. In addition, at the highest feed powder rate 30 g/min, the coating had splat-like structure. This means that the enthalpy of the plasma was insufficient to vaporise such amount of the powder. Additional 2 dm^3/min flow of oxygen to a mixture of Ar/He caused that the ceramic coating was flaking and falling off, at the lowest powder feed rate – 2 g/min. Increasing the powder feed rate to 10 and 30 g/min respectively enabled the formation of the coating characterised by the columnar structure.

Compared to the results of research conducted at the Jülich Research Centre [4, 5], there has been observed compatibility within the effect of the plasma-forming gases on the morphology of the obtained coating. The addition of H2 to the mixture resulted in the formation of less visible columns or getting splat-like layered microstructure. In the studies conducted by G. Mauer, it has been found that complete evaporation is possible at a very low flow rate of the powder (2 g/min) [4]. The results presented in this paper indicate that, except for a small feed of powder, the chemical composition of the plasma-forming gas mixture plays an equally important role. Because of the higher enthalpy plasma plume consisting of a mixture of Ar/He, it was possible to evaporate a larger amount of powder. Coatings of greatest thickness were formed at the standard plasma gas mixture, ie., Ar/He 35/60 dm^3/min. The microstructure of the coating produced with a standard gas mixture Ar/He was characterised by the greatest regularity.

Acknowledgement

This research has been funded by the Polish National Science Centre as a part of 2011/01/D/ST8/05228 research project.

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Received in January 2017