IOP Conf. Series: Materials Science and Engineering **286** (2017) 012025 doi:10.1088/1757-899X/286/1/012025

Structure and Properties of Coatings Formed by Detonation Spraying of Titanium Powder

S V Panin[1,2,3], I V Vlasov[2,3], R V Stankevich[3], D V Dudina[4,5], V Yu Ulyanitsky[4] and I S Batraev[4]

[1]Jilin University, 4026 Yatai St, Nanguan Qu, Changchun Shi, 130022, China
[2]Institute of Strength Physics and Materials Science SB RAS, 2/4, pr. Akademicheskii, Tomsk, 634055, Russia
[3]National Research Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia
[4]Lavrentyev Institute of Hydrodynamics SB RAS, 15, pr. ac. Lavrentyeva, Novosibirsk, 630090, Russia
[5]Novosibirsk State Technical University, 20, pr. K. Marksa, Novosibirsk, 630073, Russia

E-mail: svp@ispms.tsc.ru

Abstract. Structure and properties of the coatings formed by detonation spraying of titanium powder have been studied at varying the deposition parameters (nature of carrier gas, spraying distance, O_2/C_2H_2 ratio, and the volume of explosive mixture). It is shown that when air is used as the carrier gas the primary strengthening by the titanium oxide phases is realized. When nitrogen is introduced into the explosive mixture, a more complicated mechanism of hardening is realized due to the formation of titanium oxides, carbides, oxynitrides and carbonitrides. The aspects of employing the revealed "rational" modes of the detonation spraying for formation of protective composite coatings based on titanium possessing a complex of improved physical and mechanical properties are discussed.

1. Introduction

At present, several coating deposition methods are known and widely used in the industry. One of the efficient technologies for restoration, repair and strengthening of machine parts is cold gas-dynamic spraying. A key problem solved at thermal spraying is formation of protective coatings containing (new) high-strength phases [1], as well as deposition of multicomponent coatings with a uniform structure reinforced with finely dispersed inclusions (precipitations) including nanosized ones that ensures high performance properties [2, 3].

Currently, detonation spraying and high-velocity oxy-fuel spraying (HVOF) are the most efficient methods of depositing coatings that can protect machine parts from erosion, corrosion and different types of wear [4]. It advantages over the others by realizing dispersed hardening due to formation of ceramic and cermet phases which are synthesized under high temperatures during the detonation. At the same time, low porosity of the coatings is provided due to the high rate of spraying [5]. The method also might be applied for periodic restoration of worn out parts of machines [6].

High efficiency of coatings formed by detonation spraying with the use of titanium powder is worth mentioning. High temperatures and pressures to take place under the titanium deposition process give rise to formation of high-strength intermetallic, carbide and ceramic compounds. Titanium and its alloys based coatings possess high wear and corrosion resistance [7] which promotes their use in medical applications [8] as well as in aircraft industry [3].

In this paper the structure and mechanical properties of layers (coatings) formed on titanium substrates by detonation spraying of titanium powder were investigated. It is of scientific and practical interest to study the structure and mechanical properties of sprayed coatings as well as the effect of various detonation spraying parameters on the strength properties of the formed layers. Previously, the structure of such coatings has been studied in [5]. The aim of the present work is to assess the effect of the formed structure on the mechanical micro- and macroscale properties of the coatings.

2. Materials and Methods

The deposition of composite coatings onto titanium substrates was carried out using a computer controlled detonation spraying (CCDS2000) facility (table 1). Due to the interaction of titanium with the components of the spraying atmosphere, titanium oxides, nitrides, carbides, oxynitrides and carbonitrides phases were formed. Titanium (99 % purity, average particle size 15 μm, referred to as "PTOM-2", Russia) was used as a feedstock powder. Parameters of the detonation spraying for the formation of coatings are given in table 1. Microhardness of the coatings was measured on the polished surface parallel to the coating/substrate interface. Local microanalysis of the coatings was carried out by energy dispersive spectroscopy capacity INCA (Oxford, Instruments), equipped to the scanning electron microscope LEO EVO 50 (Zeiss, Germany). To establish the correlation between coating structure and mechanical properties the three-point bending tests were carried out. To this end, an electromechanical testing machine Instron 5582 was utilized. This loading scheme is motivated by the fact that under applying the external force in this way a surface layer (in this case – deposited coating) plays a major role in ensuring resistance to deformation and failure. Thus, the three-point bending testing in combination with photographing the specimen lateral surface allows one to gain more complete information on the deformation behavior as well as to estimate the cracking stress σ_{cr} [9]. The stress under the 3-point bending was calculated with the help of the formula (1) [10]:

$$\boldsymbol{\sigma_{cr}} = \frac{\boldsymbol{M_{max}}}{\boldsymbol{W}} \tag{1}$$

where $M_{\max}$ – largest value of bending moment, W – the resistance momentum for rectangular-section specimens. The shear stress was calculated by the formula (2) [11]:

$$\boldsymbol{\tau} = \frac{\boldsymbol{h_c} \times \boldsymbol{\sigma_{delam}}}{\boldsymbol{L_c}} \tag{2}$$

where L_c – the distance between the cracks in the coating, σ_{delam} – the stress at which the coating starts to delaminate (delamination stress), h_c – coating thickness. The interface fracture toughness ("coating shear resistance") was determined by the formula (3) [11]:

$$\boldsymbol{K_c} = \boldsymbol{\tau} \times (\boldsymbol{\pi} \times \boldsymbol{L_c})^2 \tag{3}$$

Specimens for mechanical testing were cut by electro-erosion machine to have the size 20×10×2.5 mm. The span (distance between the supports) was made 19 mm. Since the titanium substrate possesses high ductility, it was nearly impossible to fail the specimen under the used loading scheme. For this reason, the evaluation of mechanical properties was carried out at the bending deflection of 2.5 mm.

3. Results and discussion

For the specimen's No. 1 and 2 the spraying distance was 100 mm and filling of the barrel was 30 %. They differed by the explosive mixture ratio O_2/C_2H_2 only (table 1). Analysis of micrographs (Figure 3a,b) shows that the coating structure represents a set of densely "packed" splats that is typical for thermal spraying techniques.

This ensures low porosity and high microhardness – at a level not exceeding 3.7 MPa (table 1). The data of scanning electron microscopy, as well as the microanalysis for the coating No. 1, allows revealing two main phases being particles of titanium and its oxides. Coating No. 2 has a similar structure; however, a larger number of splat-shaped inclusions of smaller sizes are observed.

Table 1. Parameters of spraying and mechanical properties of the specimens.

Specimen No.	Composition of explosive mixture, O_2/C_2H_2	Spraying distance (mm)	Explosive charge (%)	Carrier gas	H_μ (GPa)	σ_{cr} (MPa)	K_c (MPa·m$^{1/2}$)
1	1.1	100	30	air	3.70±0.03	98.4	10.4
2	2.5	100	30	air	3.84±0.07	140.5	12.7
3	1.1	10	40	nitrogen	2.68±0.07	87.9	4.8
4	0.7	10	40	nitrogen	2.45±0.11	44.9	0.9
5	0.7	10	50	nitrogen	2.72±0.09	94.2	7.6
6	0.7	100	50	nitrogen	2.02±0.01	10	-
7	1.1+33% N_2	10	60	nitrogen	2.74±0.09	372.1	11.6
8	1.1+33% N_2	100	60	nitrogen	2.29±0.02	33.5	6.8

The microanalysis data have shown the oxygen content (specimen No. 2) in the oxide rich regions make up to 45 %, which is by ~ 10 % higher in contrast with the specimen No. 1. The key mechanical characteristics of coating No. 2 are improved relative to those of coating No. 1: the fracture initiation stress is increased by 43 % and interface fracture toughness – by 22 %, (table 1). According to the microstructure data these changes should be associated with the formation of a high strength titanium oxide based matrix.

For the specimen's No. 3 and 4 reduction of oxygen in the explosive mixture resulting in decreasing of the content of the oxidizing component in the spraying atmosphere should primarily be accompanied by diminishing the amount of oxides (Figure 1,c,d). On the other hand, the use of nitrogen as the carrier gas can be accompanied by the formation of nitride phases. The structure of the coating No. 4 is denser while its porosity is much lower (in contrast with specimen No. 3). The higher content of C_2H_2 in the explosive mixture has led to the increase in the carbon content in the coating as is evidenced from the microanalysis data (table 1).

For specimens No. 5 and No. 6, the spraying distance was 10 and 100 mm, respectively. The coatings of both types have a homogeneous fine-dispersed structure: titanium particles are surrounded by nitride, carbonitride and titanium carbide matrix (Figure 1,e,f). The increase in the deposition distance by a factor of 10 promoted the increase in the reaction time in the detonation jet and resulted in the formation of a larger number of ceramic compounds of titanium, nitrogen, and carbon. From comparison of the mechanical properties of the specimens, the following conclusions can be drawn. The thickness of the coating in specimen No. 6 was 4 times greater than that in the rest of the specimens), which significantly affected the crack resistance measured during bending and scratching (σ_{cr} and K_c). Nevertheless, the bending cracking resistance of the specimen No. 5 is higher than that of specimen No. 6. The reason might be attributed to more a uniform structure of the specimen No. 5. At the same time, the bending delamination stress of coating No. 5 (table 1) is noticeably higher than the values observed in coatings No. 3 and No. 4.

For the specimen's No. 7 and 8 the nitrogen was added to the O2/C2H2 mixture (at the ratio of 1:1) in an amount of 33 % by volume (Figure 1,g,h). It was assumed that introduction of the nitrogen into the explosive mixture would favor formation of a greater amount of nitride/carbonitride phases. It is revealed that the fracture initiation stress σcr increases by a factor of ~ 10 for the specimen No. 7 in comparison with No. 8. At the same time the interface fracture toughness Kc is increased by 40 % (table 1). A shorter deposition distance has led to increasing the oxygen content that results in the formation of larger amount of the oxide phases. The introduction of nitrogen into the explosive mixture has increased the amount of titanium nitrides and carbonitrides. The latter should be

responsible for improving mechanical properties. Generally speaking, the specimen No. 7 possesses the maximum cracking resistance among all the studied compositions.

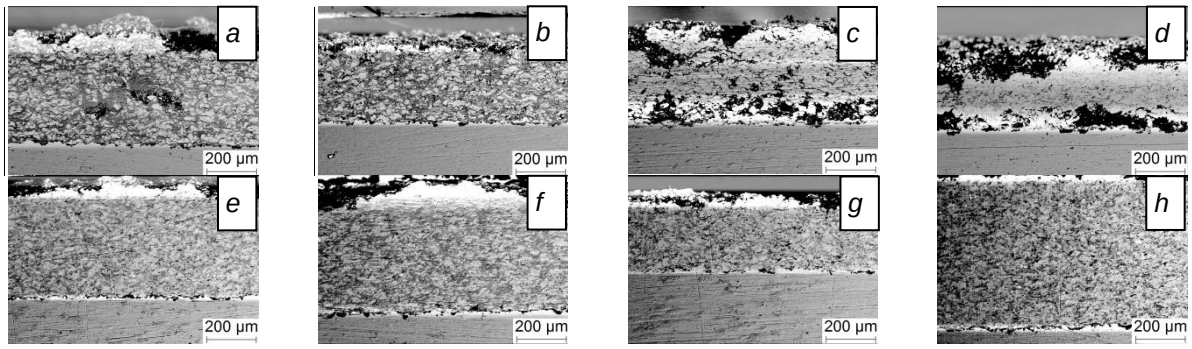

Figure 1. SEM-micrographs of the cross section for the specimens No. 1 (a); No. 2 (b); No. 3 (c); No. 4 (d); No. 5 (e); No. 6 (f); No. 7 (g); No. 8 (h).

4. Conclusion

The structure and mechanical properties of the coatings deposited by reactive detonation spraying of a titanium powder were studied. The composition of the individual phases of coatings as well as the effect of spraying regimes on the mechanical properties of the formed coatings were investigated. For the three characteristic modes of the coating formation, the following recommendations were formulated:

1. In case of the spraying with air as a carrier gas, no nitrogen added into the explosive mixture, an increase in the O_2/C_2H_2 from 1.1 and 2.5 leads to an increase in the cracking resistance under 3-point bending due to formation of a hierarchically organized coating structure with clearly exhibited phase boundaries. Deposition of titanium at O_2/C_2H_2=2.5 allows obtaining coatings with a high fracture toughness and a high microhardness;
2. In the event of spraying with nitrogen as a carrier gas, no nitrogen added into the explosive mixture, a short spraying distance (10 mm) and a low oxygen content in the explosive mixture (O_2/C_2H_2 = 0.7) makes it possible to form a heterogeneous structure of the coating. This ensures mechanical properties comparable to those of the coatings, in which the oxide phases were predominantly formed. The coatings show a moderate crack resistance and a high microhardness (H_{100} = 2.72 GPa);
3. In case of the spraying with nitrogen as a carrier gas and nitrogen added to the explosive mixture, the formation of a complex heterogeneous structure makes it possible to achieve a high crack resistance under 3-point bending, a high interface fracture toughness under the scratch test and a high microhardness (H_{100} = 2.74 GPa).

Acknowledgments

The work was partially supported by Cheung Kong Scholar of Jilin University, and performed with a partial support by Grant No. 11.2 of the Russian Academy of Sciences (Department of Power Engineering, Mechanical Engineering, Mechanics, and Control Processes). The authors are grateful to "Nanotech" Shared Use Center of ISPMS SB RAS for the assistance in running fractographic investigations. The experimental calculations are carried out at Tomsk Polytechnic University within the framework of Tomsk Polytechnic University Competitiveness Enhancement Program grant.

References

[1] Deevi S and Sikka V 1997 *Journal of Materials Science* **32** 3315-3325
[2] Fauchais P, Montavon G, Lima R and Marple B 2011 *J. Phys. D: Appl. Phys.* **44** 093001
[3] Kovaleva M, Tyurin Yu, Kolisnichenko O, Prozorova M and Arseenko M 2013 *Journal of Thermal Spray Technology* **22(4)** 518–524
[4] Smurov I and Ulianitsky V 2011 *Surface Engineering* **27(8)** 557-559
[5] Ulianitsky V, Dudina D, Batraev I, Kovalenko A, et. al. B 2015 *Surf. Coat. Tech.* **261** 174–180

[6] Senderowski C, Chodala M and Bojar Z 2015 *Materials* **8(3)** 1108-1123
[7] Zhu J, Huang J, Wang H, et. al. 2008 *Materials Letters* **62** 2009–2012
[8] Kawakita J, Kuroda S, Fukushima T, et. al. 2006 *Surf. Coat. Tech.* **201** 1250–1255
[9] Isakov M, Matikainen V, Koivuluoto H and May M 2017 *Surf. Coat. Tech.* **324** 264–280
[10] Gere J and Goodno B 2012 *Mechanics of Materials* (Canada: Cengage Learning) p 1045
[11] Zhou Y, Tonomori T, Yoshida A, et. al. 2002 *Surf. Coat. Tech.* **157** 118–127