Applied Surface Science 265 (2013) 245–249

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Deposition of titanium nitride layers by electric arc – Reactive plasma spraying method

Viorel-Aurel Şerban [a], Radu Alexandru Roşu [a,*], Alexandra Ioana Bucur [b], Doru Romulus Pascu [c]

[a] University "Politehnica" of Timişoara, Faculty of Mechanical Engineering, No. 1 Mihai Viteazu Boulevard, 300222 Timişoara, Romania
[b] National Institute for Research and Development in Electrochemistry and Condensed Matter Timisoara, Analysis and Characterization Department, No. 1 P Andronescu Street, Timisoara 300224, Romania
[c] Romania National Research & Development Institute for Welding and Material Testing Timisoara, No. 30 Mihai Viteazu Boulevard, 300222 Timişoara, Romania

ARTICLE INFO

Article history:
Received 16 May 2012
Received in revised form 27 October 2012
Accepted 31 October 2012
Available online 9 November 2012

Keywords:
Titanium nitride
Reactive plasma spraying
Electric arc thermal spraying

ABSTRACT

Titanium nitride (TiN) is a ceramic material which possesses high mechanical properties, being often used in order to cover cutting tools, thus increasing their lifetime, and also for covering components which are working in corrosive environments.

The paper presents the experimental results on deposition of titanium nitride coatings by a new combined method (reactive plasma spraying and electric arc thermal spraying). In this way the advantages of each method in part are combined, obtaining improved quality coatings in the same time achieving high productivity. Commercially pure titanium wire and C45 steel as substrate were used for experiments.

X-ray diffraction analysis shows that the deposited coatings are composed of titanium nitride (TiN, Ti_2N) and small amounts of Ti_3O. The microstructure of the deposited layers, investigated both by optical and scanning electron microscopy, shows that the coatings are dense, compact, without cracks and with low porosity. Vickers microhardness of the coatings presents maximum values of 912 HV0.1. The corrosion tests in 3%NaCl solution show that the deposited layers have a high corrosion resistance compared to unalloyed steel substrate.

1. Introduction

Components with special characteristics (mechanical properties, low density, wear and corrosion resistance, biocompatibility, etc.) are necessary in the top domains of industry (aerospace, biomedical), characteristics which are generally provided by expensive materials (titanium and its alloys, magnesium alloys and others) [1]. For this reason, surface engineering is more and more appealed in the last years, due to the good results obtainable by the components made from cheap materials and covered with materials which possess superior characteristics [2]. In this way, components with improved characteristics are obtained, but at lower costs. From the many methods used in surface engineering, thermal spraying has an increasingly applicability because of the versatility and of the wide range of materials used for deposition (metal, ceramics, cermet) [3].

Titanium nitride (TiN) is a hard ceramic material which has a very good wear and corrosion resistance [4,5], being used for coating the cutting tools to increase their lifetime [6] and also for coating the components which are working in corrosive environments such as medical implants [7]. In addition, titanium nitride has biocompatible properties [8,9], being used for covering medical implants [10]. Titanium nitride coatings can be obtained by various methods such as laser [11], reactive plasma spraying [12,13], PVD (Physical Vapor Deposition) and CVD (Chemical Vapor Deposition) [14]. The disadvantage of the PVD and CVD methods is that very small thickness of the deposited layers (maximum 10 μm) can be obtained [15]. Reactive plasma spraying (RPS) is often used for the deposition of titanium nitride layers with high quality [16], this method presenting several advantages in comparison with the CVD and PVD methods, namely: the thickness can be higher and the deposited layers present high toughness, which will provide adequate strength of the layer to shocks which can occur during the operation [17]. There are also known thermal spraying processes where the powder material for deposition is introduced into the plasma jet axis, being melted by the plasma jet, or methods where the filler material as a wire is melted by the plasma jet [18]. This last group of methods has the disadvantage that the sprayed material (wire) is melted only by the plasma jet, requiring careful attention for wire electrode positioning in the plasma jet axis, the positioning having to be in very narrow limits.

Plasma and electric arc thermal spraying process (*Plasma Jet Arc – PJA*) is our own patented invention, which eliminates the above disadvantages by concomitant introduction of the electrode wires

* Corresponding author. Tel.: +40 256494831; fax: +40 256492797.
E-mail address: raduniz@gmail.com (R.A. Roşu).

0169-4332/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2012.10.187

in the plasma jet. Between the top of the wires and the plasma jet, electric arcs are produced, which melt the electrode wire. The melted material (titanium) reacts with nitrogen from the plasmagen gas and with the nitrogen which is supplied by the wire feed gun nozzle, resulting compounds based on titanium nitride (TiN, Ti_2N). Plasma thermal spraying (RPS or APS) has a much lower coverage efficacy compared to electric arc thermal spraying method in terms of the deposited material [19]. Electric arc method, due to the high efficiency, is successfully used in order to deposit coatings with corrosion resistance (zinc, aluminum) on large surfaces [20]. The disadvantage of this method is that it is difficult to obtain quality titanium nitride layers due to the high melting temperature of titanium. Thus, combining the two methods (reactive plasma spraying and electric arc thermal spraying) only a wire filler roll of titanium can be used, obtaining high quality titanium nitride coatings due to electrical arcs which are developed and easily melt the deposition material (titanium) in nitrogen atmosphere, leading to formation of titanium nitride coatings, also ensuring a high degree of coverage efficiency.

2. Experimental procedure

2.1. Materials used

Commercially pure titanium wire (99.8%) with the diameter of 1.6 mm provided by Sulzer-Metco Company was used for the deposition of titanium nitride layers. As substrate, non-alloyed steel C45 was used. Titanium nitride coatings were achieved at four spraying distances: 100, 110, 120 and 130 mm.

2.2. Thermal spraying equipment

For the achievement of titanium nitride coatings by PJA method, an experimental installation has been developed, composed of a Sulzer Metco plasma thermal spraying equipment with 3BM spraying gun, where the wire electrode (titanium wire) is introduced into the plasma jet by an MIG/MAG (Metal Inert Gas/Metal Active Gas) welding installation. Between the top of the wire electrode and the plasma jet an electric arc is produced, which is powered by Sulzer Metco/LCARE Value Arc 200 electric arc spraying source. The electric arc produced between the wire electrode and the plasma jet burns in nitrogen atmosphere supplied through a MIG/MAG nozzle gun. Fig. 1 shows the schematic representation of the thermal spraying process. The steel substrates (C45) before thermal spraying operation were blasted with alumina particles with the average particle size of 1 mm at the pressure of 6×10^5 Pa. After blasting the samples were cleaned with ethylic alcohol and were deposited immediately in order to avoid the oxidation of the blasted surfaces.

Plasma Jet Arc thermal process does the spraying of the wires electrode *1* melted by the electric arc *2* and by plasma jet *3*. Plasma jet directs the molten metal particles *4* and projects them with high speeds, the coating *5* resulting on the substrate *6*. The electric arc is powered by the power source *7* and burns between the top of the wire electrode and the plasma jet into the reactive gas environment *8*. The plasma jet is produced by the electric arc *9* which burns between the electrode (cathode) *10* and the nozzle (anode) *11*, powered by the power source *12*, constrained by the nozzle and projected with high speed by the gas stream *13*. Technological parameters of plasma thermal spraying and electric arc processes are presented in Tables 1 and 2.

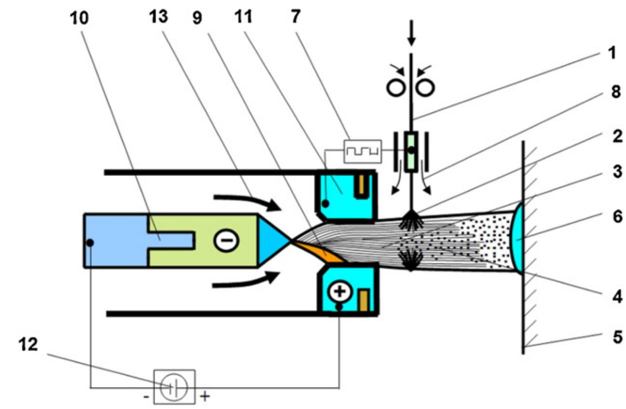

Fig. 1. Principle of obtaining titanium nitride layers by PJA thermal spraying method.

Obtaining plasma jet using pure nitrogen is very complicated due of the high ionization potential of nitrogen [21]. In these conditions, the plasma jet ignition was performed using a two-way valve. The plasma jet was achieved initially with Ar + 6%H_2 mixture, and after the plasma jet was obtained and stabilized, the valve was changed to nitrogen.

2.3. Characterization of surface morphology

Scanning electron microscope (SEM) Inspect S with Energy-Dispersive X-ray (EDX) spectroscopy was used to characterize the surfaces morphology. The phase composition of the deposited layers was investigated by X-ray diffraction (XRD) using a PANalytical X'Pert Pro MPD diffractometer at 45 kV and 30 mA, using copper radiation with the wavelength λ = 1.541 Å and the calculations were performed using the dedicated software of the equipment. For hardness (HV) measurements the ZWICK 3212 device was used, Easy Check F-N device was used for coatings thickness determination and Surftest 201 (SJ-201) was used for the determination of the surface roughness.

3. Results and discussion

3.1. XRD characterization

Fig. 2 shows the X-ray diffraction pattern of titanium nitride coatings deposited by PJA spraying method.

Table 1
Plasma jet parameters.

Plasmagen gas	Plasma current (A)	Plasma voltage (V)	Breakdown voltage (V)	Primary gas flow (l/min)	Plasmagen gas pressure (bar)	Spraying distance (mm)	Cooling
Nitrogen	650–670	60–65	150	40	7	100–130	Nitrogen

Table 2
Wire arc–plasma jet parameters.

Gas	Current (A)	Arc voltage (V)	Breakdown voltage (V)	Nitrogen gas flow (l/min)	Arc-plasma nozzle distance (mm)
Nitrogen	65–70	4–5	150	30	15