Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Comparative study of Ti-C-Ni-Al, Ti-C-Ni-Fe, and Ti-C-Ni-Al/Ti-C-Ni-Fe coatings produced by magnetron sputtering, electro-spark deposition, and a combined two-step process

Ph.V. Kiryukhantsev-Korneev*, A.N. Sheveyko, N.V. Shvindina, E.A. Levashov, D.V. Shtansky*

National University of Science and Technology "MISIS", Leninsky prospect 4, Moscow, Russia

ARTICLE INFO

Keywords:
Ti-C-Ni-Al and Ti-C-Ni-Fe coatings
SHS electrodes
Magnetron sputtering
Electro-spark deposition
Mechanical and tribological properties
Oxidation and corrosion resistance

ABSTRACT

Comparative study of Ti-C-Ni-Fe, Ti-C-Ni-Al, and Ti-C-Ni-Al/Ti-C-Ni-Fe coatings obtained by electro-spark deposition (ESD) using TiCNi electrode, magnetron sputtering (MS) of TiCNiAl target, and a combination of these methods (MS-ESD) was carried out. The coating microstructures and elemental compositions were studied by means of X-ray diffraction, scanning electron microscopy, energy-dispersive spectroscopy, and glow discharge optical emission spectroscopy. The materials were tested in terms of their hardness, elastic modulus, elastic recovery, crack resistance, friction coefficient, and wear resistance under sliding, impact and abrasive conditions, as well as corrosion- and oxidation resistance. The work demonstrated that the utilization of a combined two-step MS-ESD technology permits to obtain bilayers made of Ti-C-Ni-Al/Ti-C-Ni-Fe coatings with improved crack-, wear- and oxidation resistance compared with their single-layered Ti-C-Ni-Al counterparts deposited by MS, and with reduced friction coefficient and enhanced corrosion resistance compared with ESD Ti-C-Ni-Fe coatings.

1. Introduction

Friction and wear cause essential energy and financial losses, therefore the development of new types of wear-resistant coatings is one of key topics in surface engineering. Ceramics possess a good combination of properties, such as high hardness, wear-, corrosion- and oxidation resistance, but high brittleness restricts their widespread use as load-bearing components. In contrast, metals and alloys have a high durability, plasticity, fracture toughness, and tensile strength, but suffer from limited hardness. The advantages of the two material classes can be combined in a single metal-ceramic bulk material or coating known as cermet. WC-Co is one of the most famous representatives of cermet coatings. Although the first results describing WC-Co coatings were published as far back as in the 1960s [1], the material was widely investigated in subsequent years [2,3] and the interest in it has remained till now [4]. In total, several thousand articles on WC-Co coatings have been published so far. A complete review of earlier results on WC-Co coatings was published in 1998 [5]. WC-Co coatings revealed a good combination of properties, but further development of cost-effective industry requires replacement of expensive tungsten with more affordable materials. To meet these requirements, different tungsten-free materials were developed and manufactured, for example TiC-Ni, which is a good alternative to the WC-Co cermets.

To date, Ti-C-Ni-based coatings were prepared by different technologies including cladding (arc welding) [6], vacuum plasma- and high velocity oxygen fuel spraying [7], as well as laser treatment [8]. Ti-C-Ni-Cr coatings with metal matrix reinforced with TiC particles were successfully deposited by cold spray technology [9]. Nanocomposite Ti-C-Ni coatings obtained by magnetron sputtering and cathodic arc evaporation demonstrated hardness as high as 27 GPa, low friction coefficient 0.15–0.20 and high thermal stability up to 900 °C [10–12]. Electro-spark deposition, also often called electro-spark alloying, is a relatively simple vacuum-free and cost-efficient technology that permits to produce a coating with high thickness, continuity, increased surface roughness, as well as desired chemical and mechanical properties, either in air or in a protective environment. This method was successfully utilized to deposit cermet-based protective coatings. For example, electro-spark deposited Ti-C-Ni coatings were successfully used to improve surface characteristics of Ti alloys [13]. Note, however, that the electro-spark deposition has not been used so far for the protection of steels *via* deposition of Ti-C-Ni coatings.

One of the main advantages of the electro-spark deposition is that the method provides superior adhesion between coating and substrate due to chemical mixing of the melted substrate with the deposited material transferred from the electrode during spark discharge [14–16]

* Corresponding authors.
E-mail addresses: kiruhancev-korneev@yandex.ru (P.V. Kiryukhantsev-Korneev), shtansky@shs.misis.ru (D.V. Shtansky).

https://doi.org/10.1016/j.ceramint.2018.01.187
Received 7 November 2017; Received in revised form 22 January 2018; Accepted 22 January 2018

and short-term thermal effects on the substrate due to pulsed power supply [17,18]. Electro-spark deposited coatings (hereafter referred to as ESD coatings/sublayers) with high erosion- [19,20], wear- [21], oxidation- [22], and corrosion resistance [23,24] were reported.

The shortcomings of ESD coatings include high surface roughness, which, however, can be an advantage for certain applications, and a high concentration of defects such as micro-cracks and pores. For example, the formation of micro-cracks and delaminations in ESD Ti-C-Ni coatings due to a high tensile thermal stress was reported [25]. This disadvantage can usually be eliminated by additional post-treatments. Bejar *et al.* [26] applied ESD and then carried out plasma nitriding. The subsequent laser treatment of ESD WC-based coatings was shown to decrease roughness and heal defects; as a result, the friction coefficient was decreased from 0.8 to 0.6 [27]. The vacuum ion etching can also be utilized to reduce the surface roughness of ESD coatings [28]. Another approach is a deposition of a thin film using an atomized material flow capable of healing defects and covering microcracks on the surface of ESD coating. Thus the development of a technology which combines two processes, *i.e.* electro-spark deposition and magnetron sputtering, is of great scientific and practical interest.

The main advantage of magnetron sputtering is that a coating of the desired composition can easily be deposited onto the surface of different substrates, such as metals and alloys [29], composite and ceramics [30], organic materials [31], polymers [32], and textile [33]. Coatings deposited by magnetron sputtering (hereafter denoted to as MS coatings) do not significantly change the substrate surface topography and roughness [34,35]. In addition, MS coatings usually have a low defect density and a dense homogeneous structure with uniform elemental distribution through the coating thickness [36]. High adhesion strength can be achieved by increasing the ionic component in the atomic flow [37,38]. Thus, the magnetron sputtering can be combined with electro-spark deposition to improve the quality and functional properties of the coatings.

The present study aimed at developing duplex coatings in which the bottom Ti-C-Ni-Fe layer obtained by electro-spark deposition using TiCNi electrode and adjacent to steel substrate has a relatively high thickness and toughness, whereas the top Ti-C-Ni-Al layer fabricated by magnetron sputtering of TiCNiAl target has enhanced tribological properties and high corrosion resistance. The chemical, mechanical, and tribological characteristics of such duplex coatings are compared with their single-layer Ti-C-Ni-Fe and Ti-C-Ni-Al counterparts. The choice of the sublayer composition (Ti-C-Ni-Fe instead of Ti-C-Ni-Al-Fe) is explained by the need to avoid the formation of intermetallic phase which decreases the fracture toughness.

2. Materials and methods

Ti-16%C-20%Ni (44.3 at% of C and 11.4 at% of Ni) and Ti-16%C-14%Ni-6%Al (42.5 at% of C, 7.5 at% of Ni, and 7.5 at% of Al) materials for electro-spark deposition and magnetron sputtering, respectively, were synthesized from the exothermal powder mixtures using the combined force SHS-pressing technology, as described elsewhere [39]. A TiCNi electrode (with a square section of 4 × 4 mm^2 and a length of 60 mm) and TiCNiAl target (disc ø120, thickness 7 mm) were cut from the central parts of the synthesized billets using an electroerosion machine. Polished 40X steel disks (analog of 5135 steel, 58 HRC), 30 cm in diameter, with an average surface roughness (Ra) of 16 nm were used as substrates. Before coating, the substrates were ultrasonically cleaned in isopropyl alcohol for 5 min using an UZDN-2T machine operating at a power of about 100 W and a frequency of 22 kHz.

Electro-spark deposition was performed in an Ar atmosphere at a total pressure of 10^5 Pa with an Alier 303 Metal power supply unit having direct polarity of connections of the electrode (anode) and the substrate (cathode) using the following processing parameters: current of 120 A, voltage (open circuit) 20 V, pulse duration 20 μs, frequency 640 Hz, duty cycle 1.3%, and deposition time 3 min/cm^2. The deposition parameters were chosen to ensure a minimal surface roughness (Ra = 8 μm). A part of ESD coatings (hereafter designated as ESD_{pol} coatings) was additionally polished to reduce the roughness to 0.1 μm using a Struers Rotopol machine. The samples with ESD coatings were used for subsequent deposition of Ti-C-Ni-Al coatings using magnetron sputtering.

The Ti-C-Ni-Al coatings were formed by DC magnetron sputtering (current 2 A, voltage 500 V) of TiCNiAl target in a pure Ar using a UVN-2M vacuum unit (Russia). Substrates were mounted on a 2-axis rotating table equipped with a bias voltage supply system, a heater, and a thermo-couple for temperature control. Before coating, substrates were additionally etched in a vacuum chamber using Ar^+ ions with an average energy of approximately 2 keV for 20 min using a slot-type ion source. The distances from the target and ion source to the substrate were 9 and 13 cm, respectively. The total pressure was maintained at 0.2 Pa. During deposition, the negative substrate bias voltage was kept constant at −250 V to ensure both high adhesion strength and better separation between phase constituents due to high adatom mobility.

The microstructure of coatings was examined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) using a S-3400N Hitachi microscope equipped with a Noran 7 Thermo Scientific spectrometer. X-ray diffraction (XRD) patterns were recorded using a D8 Advance X-ray diffractometer (Bruker) with CuKα monochromatic radiation. The XRD data were recorded in the range of 20–80 (2θ deg) in the conventional Bragg-Brentano geometry. The depth distribution of elements in the coatings was obtained by glow discharge optical emission spectroscopy (GDOES) using a PROFILER 2 instrument (Horiba Jobin Yvon) [40].

The coatings were characterized in terms of their hardness, effective Young's modulus, and elastic recovery using a nano-hardness tester (CSM Instruments) equipped with a Berkovich diamond indenter tip under an applied load of 8 mN. The hardness and effective Young's modulus were calculated using the Pharr and Oliver method [41]. A pin-on-disc tribometer (CSM Instruments) was employed for the evaluation of coating tribological characteristics. The samples were tested against a 3-mm diameter 440c steel ball at a linear speed of 10 cm/s under a normal load of 1 N. Fracture toughness and impact resistance of the coatings were studied using a "ball-on-plate" impact tester (CemeCon). The samples were subjected to a range of impacts at a constant impact frequency of 50 Hz using a cemented carbide ball with 5-mm diameter. Deformation area was cooled by compressed air. Each sample was subjected to tests at 500 N for 10^5 cycles. Coating abrasive resistance was estimated using a calowear-tester NIITAvtoprom. The 100Cr6 steel ball, 27 mm in diameter, was used as a counterpart material. The slurry containing 15-μm-sized diamond particles (Struers) was applied to the sample surface before tests. The applied load and ball rotation speed were kept constant at 3 N and 153 rev/min, respectively, for the whole duration of the tests lasted for 5 min. An optical profiler WYKO-NT1100, an optical microscope Axiovert, and a Hitachi S-4800 scanning electron microscope were used to observe the shape and morphology of impact cavities, abrasive craters, and wear tracks. Optical profiler was also used for estimation of coating roughness.

Electrochemical measurements were performed in a three-electrode cell with a VoltaLab 50 potentiostat (Radiometer Analytical). The tests were carried out in 1N H_2SO_4 solution using an Ag/AgCl reference electrode and a Pt disc counter electrode. The samples were fixed in a holder with a window of ~1 cm^2 for interaction with the electrolyte. Open-circuit corrosion potentials (OCPs), E_{corr}, were measured as a function of time for 1 h until a stationary state was reached. Potentiodynamic polarization measurements were performed over the potential range from −0.2 to 3.0 V with respect to the open-circuit potential at a scan rate of 1 mV/s. All potentials were recalculated with respect to the standard hydrogen electrode. Corrosion current density (I_{corr}) was obtained using Tafel calculations.

The coating oxidation was studied at room humidity (< 30%). The