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Ion treatment by low pressure arc plasma immersion surface engineering processes

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ABSTRACT

The gaseous plasma of low pressure arc discharges has been used extensively for various surface treatment applications including heat treatment, ion nitriding, ion implantation, PECVD and duplex processes. Highly ionized low pressure arc plasmas with electron density up to ~10^{18} m^{-3} can be generated by a shielded vacuum arc cathode, a hollow cathode or by a thermionic cathode. In this paper, plasma properties are characterized by electrostatic probes and optical emission spectroscopy. A range of different species can be produced in low pressure arc plasma immersion processes via decomposition of precursor molecules by electron collisions. Surface treatment of different steels and metal alloys in such a dense plasma environment can substantially affect the surface profile. The ion nitriding of different types of steel in a low pressure arc plasma environment is investigated. The rate of ion nitriding as a function of plasma parameters, such as ion current density, pressure and gas composition is established for several types of steel and ranging from 0.1 to 1 μm/min. Ionitrided layers can be produced in arc plasma immersion processes at substrate biases as low as −30 V and substrate temperatures as low as 200 °C, depending on the type of steel. Alternatively, low energy ion implantation of nitrogen can be produced at bias voltages exceeding −500 V and substrate temperatures less than 100 °C. The distribution of plasma density and the uniformity of ion nitriding layers in industrial scale vacuum processing chambers are investigated. Duplex coatings were also produced by ion nitriding in an arc plasma immersion environment followed by deposition of TiN coatings. The ion nitriding and duplex coating layers are characterized by structure, thickness, microhardness depth profile, surface roughness and coating adhesion. Surface treatment in conventional glow discharge compared to low pressure arc plasma immersion processes is presented. The results of processing complex shape components are discussed.

1. Introduction

For the past 20 years, plasma immersion surface engineering technologies have been under increasing attention of the scientific and industrial communities. Following the pioneering work of Conrad [1] who introduced plasma immersion ion nitriding, it is now successfully applied to other processes, like ion implantation, ion cleaning, and coating deposition [2]. The basic approach of this technology is to split up two different tasks: creation of a plasma environment and providing ion bombardment of the substrates by the ions attracted from the surrounding plasma. In a traditional technology a high voltage bias is applied to the substrates, which creates anomalous glow discharge plasma surrounding the substrates. At the same time, the same bias voltage is used to attract the ions from the plasma. The characteristic pressure for glow discharge ion nitriding technology is 1–10 hPa, as determined by Paschen curve [2,3]. Plasma source ion nitriding and low energy ion implantation use an independent plasma source to ionize a nitrogen containing reactive gas atmosphere and then deliver a high flux of highly chemically active nitrogen-bearing atomic particles to the substrate surface [2]. The flux of nitrogen ions can be formed by ion beams as in the case of ion beam nitriding of titanium alloys in [4]. Alternatively a set of active nitrogen-bearing species can be generated by different plasma discharges such as glow discharge, MW (microwave), RF or DC arc discharge [2,5–7]. Low temperature ion nitriding and ion implantation processes can be performed in highly ionized dense plasma environments [2,5,8–10]. In the case of plasma immersed ion nitriding processes, the operating pressure is determined by an independent plasma source, while the bias potential applied to the substrate can be varied over a wide range, independently from the plasma generator. In most cases, RF or thermionic DC plasma sources were used to generate the plasma environment for plasma immersed processes. At the same time it was found that using a cold vacuum arc cathode to generate a plasma environment yields significant advantages over other electron emitters such as hollow cathodes or thermionic cathodes for plasma immersed processes [11–18]. The first experiments using vacuum cathodic arc sources integrated in conventional cathodic arc coaters were conducted in the 1980's–1990's to generate a remote arc discharge (RAD) plasma also known as arc enhanced glow discharge (AEGD) for ion nitriding, ion cleaning, ion implantation and coating deposition processes [19–24]. In this approach the

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dense and highly ionized plasma of the positive column of the remote low pressure arc or glow discharge is generated between the cathode of the primary vacuum arc discharge and the remote anode. It was found that vacuum arc generators are capable of providing a uniform distribution of dense and strongly ionized gaseous plasma over large industrial coating chambers. In addition, the cathodic arc source can operate in any reactive gaseous environment which makes this type of plasma generator more widely useful than hot filament or hollow cathode thermionic cathodes.

Low temperature and low pressure plasma immersion surface modification processes are also capable of supporting duplex surface treatment which consists of the combination of ion diffusion saturation of the surface layer followed by hard thin film coatings [2,14–17,20–27]. This approach is particularly effective in improving the load bearing capacity of surfaces. Thin film surface coatings deposited by PVD and CVD techniques are hard and can provide excellent tribological properties, but when they are deposited on a relatively soft metal substrate experiencing large plastic deformation at high loads, the egg-shell effect can reduce the load bearing capacity of the coated surface hence limiting its wear resistance [14,15,17,26–28]. Super hard DLC (diamond-like carbon) coatings have unique tribological properties with microhardness >50 GPa and coefficients of friction <0.1 at small loads $P<P_c$. However, when the DLC layer is deposited on relatively soft metal substrates it shows a rubber-like elastic behavior with negligible plastic deformation. When the substrate experiences large plastic deformation at increased loads $P>P_c$ the DLC layer collapses. The value of the critical load, P_c, increases both with substrate hardness and with thickness of the coatings. For the loads larger than $P_{c,}$ a macro failure of the coating over an area considerably larger than the indentation region is observed [14,15]. Duplex surface engineering is aimed at reducing the sharp gradient between the hard thin film coating and the soft metal substrate. The ratio of hard coating thickness to the thickness of the surface layer with improved hardness, such as an ion nitrided or a carburized layer may exceed 1:10 to achieve optimal results for load bearing capacity. This technique was applied to DLC coatings deposited on steel substrates in [14,15]. In these works, two coating layers, a 0.5 μm thick layer of DLC having hardness >75 GPa, and a 0.5 μm thick layer of TiN, having a hardness of 30 GPa were deposited on top of steel with a 30 μm ionitrided layer, having a hardness of 13 GPa, creating a nitrided steel-superhard coating system with improved load bearing capacity. It was shown in [26] that while untreated titanium and its alloys can hardly sustain 0.1 GPa at $<5\%$ sliding–rolling ratio, the novel titanium duplex system combining an oxygen diffusion treatment with a DLC coating can withstand 1.7 GPa under 100% sliding conditions. A similar approach was used in [27] where duplex surface engineered systems consisting of a nickel diffusion layer followed by TiN and DLC coatings were optimally designed and successfully tested.

Duplex coatings are found to improve wear resistance in large contact load applications when failure of the substrate system is by the egg-shell effect; effectively, a relatively soft metal substrate is unable to support a thin hard coating and under high loads the coating fails. In such cases the ion nitrided layer which has a hardness intermediate between a hard coating and a steel substrate can be adjusted to smooth the gradient in hardness distribution across the near-surface layer. Ion nitrided intermediate layers can also contribute to the improvement of corrosion resistance both in low temperature and in high temperature applications. Die casting dies have to survive a highly aggressive environment in an Al–Si foundry process. Duplex coatings on this tooling, deposited in the LAFAD system, were successfully utilized. In this application TiB_2-containing multilayer coatings deposited by the filtered arc process on ion nitrided steel have demonstrated an order of magnitude improvement over samples which had only a coating or only an ion nitrided surface. This is due to the improvement in the strength and surface hardness of the substrate as well as diffusion barrier behavior provided by the combination of ceramic coatings and ion nitriding [21–24].

In the present work, ion treated surfaces of different steel produced in nitrogen and argon–nitrogen RAD plasma immersion processes are studied with emphasis on correlations between plasma characteristics and surface properties during initial stages of plasma-surface interaction. The modeling of nitrogen surface diffusion at the initial exposure of the steel substrate in a low pressure RAD plasma environment is discussed. This model is limited to the time until nitrogen concentration in a surface layer reaches its solubility limit. The modification of surface properties of different types of steel due to ion treatment in low pressure RAD plasma at later stages of the process is also discussed mostly for demonstration of the potential of this technology. Hardening of surface layer, formation of compound layer and examples of duplex coatings are also presented for illustration purposes, but detailed kinetics of RAD plasma ionitriding during later stages of the process (after surface reaches the nitrogen solubility limit) and functional properties of the RAD plasma treated surfaces are not discussed in this preliminary paper, which will be a subject for the further works.

2. Experimental details

A schematic illustration of the Large Area Filtered Arc Deposition (LAFAD) surface engineering system used in this study is shown in Fig. 1. It has a main chamber 600 mm dia × 600 mm height with an attached Large Area Filtered Arc Source (LAFAS). This unidirectional dual filtered arc plasma source has a rectangular plasma guide chamber with two cathodic arc sources attached to the opposite walls of the plasma guide chamber. Each cathodic arc source utilizes a cylindrical "billet"-like target, 80 mm dia × 50 mm long. The plasma guide has a deflecting, focusing, and scanning magnetic system which allows the plasma jet to be turned by 90° and focused toward the substrate to be coated. The positions of the cathode targets are displaced to each other by 50 mm in the vertical direction to compensate for the centrifugal drift of the vacuum arc plasma jets in a curvilinear magnetic field [14–17,20,22,29,30]. The remote anode is installed in the coating chamber opposite to the LAFAS opening. This allows operating in two modes: first, in a gaseous plasma processing mode and second, in filtered cathodic arc deposition mode. In gaseous plasma processing mode the deflecting magnetic field of the LAFAS is turned off which makes it a powerful source of electrons emitted by the cathodes of the primary arc sources. The influx of electron current propagating from the primary cathodic arc throughout the coating chamber creates highly ionized plasma on its way toward the remote arc anode. In the coating deposition mode, the magnetic deflecting field of the LAFAS is turned on bending the metal vapor plasma flow toward substrates to be coated in the coating chamber. The array of conventional tubular resistance heaters is set between the substrate holder platform and the auxiliary anode surrounding the substrate fixtures set. The coating deposition area of the system is 450 mm dia × 350 mm height. The substrate platform has 12 satellites, which can be provided with single or double rotation. The steel disks used as substrates for all trials were installed on a satellite position with single and double rotation [20,29,30].

The typical LAFAD plasma processing parameters used in most of the deposition trials reported in this work include the following steps: after pre-heating to 300–350 °C using a radiant heater array, the substrates were subjected to fifteen or twenty minutes of ion etching at ~0.1 Pa in an argon RAD plasma generated by the LAFAS with the deflecting magnetic field turned off. After the ion etching step, nitrogen was added to the gas atmosphere at pressures ranging from 0.02 to 1 Pa and to carry out the ion nitriding stage. For the duplex treatment, filtered arc coatings of different architectures were deposited after the ion nitriding stage. During deposition of ceramic or cermet coatings, an ultra-thin metallic bond layer is deposited first to improve the coating adhesion. The metal coatings were deposited in argon, while during deposition of carbides, nitrides or oxiceramic layers, a reactive gas (methane, nitrogen and/or oxygen)