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Publication Date

2003-10-29

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“Nouvelles Tendances en Procédés Magnetron et Arc pour le Dépôt de Couches Minces”

A joint workshop of the Belgian and French Vacuum Society

Gent, Belgium, November 24-25, 2003

Cathodic Arcs

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Abstract

Cathodic arc plasma deposition has become the technology of choice for hard, wear and corrosion resistant coatings for a variety of applications. The history, basic physics of cathodic arc operation, the infamous macroparticle problem and common filter solutions, and emerging high-tech applications are briefly reviewed. Cathodic arc plasmas stand out due to their high degree of ionization, with important consequences for film nucleation, growth, and efficient utilization of substrate bias. Industrial processes often use cathodic arc plasma in reactive mode. In contrast, the science of arcs has focused on the case of vacuum arcs. Future research directions include closing the knowledge gap for reactive mode, large area coating, linear sources and filters, metal plasma immersion process, with application in high-tech and biomedical fields.

Introduction

As the name suggests, cathodic arcs are determined by cathode processes. Arc processes are fundamentally different than cathode processes of more “moderate” forms of discharges, e.g. glow or magnetron discharges. Current densities, and associated power densities at cathode spots are extremely high, and this is true despite the characteristic low cathode fall voltage of typically 20 Volts. The electron emission processes involve violent, non-stationary phases, leading to the destruction of the electron emission center. The phase transition from the solid cathode material to plasma enables operation of the arc discharge and makes cathodic arcs plasma deposition possible.

The instantaneous plasma pressure in cathode spots exceeds atmospheric pressure by orders of magnitude. It is therefore not surprising that cathode processes observed for vacuum arcs also apply for arc discharges in the presence of gas between electrodes. The gas, though, has also secondary effects, especially on the surface conditions of the cathode. The arc cathode can

also operate in other modes, in particular in the thermionic mode, characterized by thermionic electron emission which occurs at very high cathode temperature. Additionally, the anode is not always a passive electron collector but may emit anode vapor and plasma ("anodic arcs" [1]). Here, the focus is on cathodic arcs with globally cold cathodes, where plasma is produced at non-stationary cathode spots.

Cathodic arc plasma deposition is a coating technology whose potential is not fully utilized. Arc plasmas are fully ionized with very energetic ions, promoting adhesion and the formation of dense films, which can have advantageous implications for hardness, elasticity, refractive index, etc. However, there are also disadvantages and problems. Films may be under excessively high compressive stress, which can lead to delamination, but most importantly so-called "macroparticles" may be incorporated.

The remainder of this brief overview will address a number of these issues, including the history and physics of cathode processes, plasma parameters, macroparticle filtering, film formation by energetic condensation, bias techniques, the issue of arcing, and some applications.

A few remarks on the history of cathodic arcs

The history of cathodic arc plasma deposition may be traced back to the 18th century. The observation of pulsed and later continuous discharges is closely related to the invention of suitable electrical storage means, namely the capacitor (Leyden jar) and electrochemical battery (Voltaic pile). Based on discharges of capacitor banks, Joseph Priestley observed the formation of coatings on glass as early as 1766. Continuous arc discharges were made by Vasilii Petrov in St. Petersburg (1803) and independently by Humphry Davy in London (about 1808). Both researchers used very large Voltaic piles. The circumstances of these developments were the subject of recent publications [2,3].

Much understanding was gained by Michael Faraday's discovery of electromagnetic induction (1831) and James Maxwell's theory of electromagnetism (1873). First practical applications of cathodic arc coatings were patented by Thomas Alva Edison [4,5].

Cathodic arcs remained a subject of research with tough challenges, with application in switching rather than coating. Researchers such as Tanberg [6] developed clever techniques to uncover the secrets of cathode spot physics. As part of the Manhattan Project, vacuum arcs were

investigated in the 1940s for uranium isotope separation, although ultimately the arc centrifuge was not used.

With the growth of post WWII industrial demands, cathodic arc coating technology was rediscovered. Arc plasma sources for DC operation were developed, especially in the former Soviet Union. Of particular importance were the patents by Snaper [7] and Sablev and coworkers [8] because they describe the basic design of these sources. DC arc sources were used by leading companies like Multi-Arc who first replicated and later improved Soviet arc technology. More details will be available in a future publication [9].

The physics of cathode processes

Cathode processes are at the heart of cathodic arc plasma deposition. The plasma "root" or "attachment" on the cathode is localized in micron-size spots that move randomly or magnetically steered on the surface. A central quantity is the current density of cathode spots. It is important because the current density distribution determines the power density distribution, which, in turn, governs all processes of electron emission, phase transitions, and plasma production.

There is evidence for a cathode spot structure containing interacting activity centers called *fragments* ([10] and references therein). The current density of cathode spot is of order 10^8 A/cm^2, with possibly even high peaks at fragments, and somewhat lower values if averaged in time and over the spot-surrounding area. Since the area of a spot is difficult to define, the current density as a single value may be ill defined; and it may be better to use the concept of a space and time-dependent current density distribution. Even when using the simplified current density approach, we realize that the associated areal power density is of order 10^9 W/cm^2 because the cathode fall is of order 20 Volts. This power density is sufficient to transform cathode material from the solid to the plasma phase in 10-100 ns [10]. It is appropriate to call a phase transition of such short duration an explosion. Fluctuations on longer time scales also appear due to the statistical superposition of numerous elementary events. The fractal model appears to be a good approach to a more comprehensive understanding, which is still waiting to be worked out.

Explosive phase transformation is characteristic for cathodic arcs [10,11]. None of the traditional, stationary electron emission mechanisms (thermionic emission, field emission, Schottky-enhanced thermionic emission) is responsible but "explosive electron emission"

[12,13]. Electrons are emitted by the synergetic presence of high temperature, high electric field, and via ionization of cathode material. Cathode spots have to fulfill the function of electron emission centers *and* provide the condition for self-sustained arc operation through plasma generation. The presence of dense metal plasma "squeezes" the cathode fall voltage into an extremely thin layer, thereby localizing power dissipation.

A micro-explosion is changing the surface topography and is rapidly heating the zone beneath the spot. Besides changes of the local conductivity, the spot area will increase with time due to heat conduction, which makes the phenomenon inherently time dependent. An increasing area implies a decreasing current density and power density. The amount of cathode material transferred by the explosive phase transition will become less in time. Therefore the cathode fall will be less "squeezed" to the surface. The electric field strength and power density will decrease further with time, reducing electron emission. The peak temperature will also fall, and hence electron emission will gradually cease. The spot activity will go from its nanosecond "explosive" phase to a slower "evaporative" phase. The discharge will completely cease unless a new center is formed by a new microexplosion. What appears as macroscopic "motion" of the cathode arc spot is more accurately described as a rapid sequence of ignition and extinction of active spots at different locations.

Due to the extremely high power density, the metal plasma produced in the explosive phase is fully ionized and often contains multiply charged ions. Charge state distributions of cathode arc plasmas in vacuum have been extensively studied (e.g. [14-16]).

Driven by the very high pressure gradient near the spot, in conjunction with electron-ion coupling, ions are accelerated to supersonic velocities in the order of 10^4 m/s. Velocity distribution functions [17,18] for the vacuum case are characterized by one dominant peak rather than charge-state-dependent values, which points to the collective, hydrodynamic nature of ion acceleration.

The parameters of cathode processes depend greatly on the surface state, especially on the presence of non-metallic layers such as of oxides, nitrides, hydrides, carbides, and hydrocarbons, which depends on vacuum quality, treatment history, and temperature [19]. If an arc is burned on a non-conditioned, "fresh" cathode surface, the current per emission center, or arc spot, is much smaller than the current per spot in the case of a chemically clean metal surface. In the present of a non-metallic layer, craters produced by arc spots are smaller and

separated from each other. In contrast, craters on clean metal surfaces are larger and form continuous chains. Traditionally, the spots are called of type 1and 2, respectively. One can easily remember this order: an arc starts burning with type 1 spots; the action of ion bombardment and heat cleans the surface and the spot transitions to type 2.

The amount of plasma produced was found to be directly proportional to the arc discharge current [20]. Other parameters such as burning voltage, ion velocity, and mean ion charge state do *not* noticeably depend on the arc current. This may be surprising at first sight. It becomes plausible if one considers that higher currents lead to "spot splitting" or a larger *number* of simultaneously active cathode spots, where each of the spots maintains the same operational mechanism.

Using the physical framework of wire-explosions, Mesyats introduced the concept of a minimum action that is needed to achieve electron emission via the explosive mechanism. He termed the elementary explosive event "ecton" [13].

Interelectrode plasma

Ion acceleration is mainly due to the electron and ion gradients which are strongest right at the cathode spot. The vacuum arc plasma drift velocity is approximately constant when the plasma travels to the substrate unless gradients of a magnetic field cause changes [21]. If a cathodic arc is operated in a gas, ions may suffer collisions with gas molecules and therefore slow down. Ionization of background gas and reduction of ion energy depend on the pressure and type of gas. As a rule of thumb, if the background pressure approaches or exceeds 1 mTorr (0.1 Pa), the mean free path becomes smaller than the size of the coating system, and thus a strong influence of the gas can be expected. For free expansion, i.e. expansion not dominated by external magnetic fields and interaction with gas, the plasma density falls as d^2, where d is the distance from the cathode spot [20]. The more the plasma expands, the lower its density and associated deposition rate, but the larger the area that can be relatively uniformly coated.

The collision rates in an expanding vacuum arc plasma drop rapidly. The rate for inelastic collisions becomes negligible at small distances from the cathode spot, and therefore the ratios of ion charge states are practically constant in the expanding plasma. The plasma is in ionization non-equilibrium and exhibits a "frozen" (i.e. constant) charge state distribution [16]. In the presence of background gas, or strong external magnetic fields, the model of a frozen charge

state distribution does not apply. The background gas can be ionized through electron impact ionization and charge exchange collisions. The ionization of background gas is greatly enhanced if a magnetic field is present because the path length of electrons is multiplied through gyro-motion.

Macroparticles

Macroparticles are liquid or solid debris particles that are produced at cathode spots. Jüttner [22] explained particle formation through the action of plasma pressure on the melted cathode material that is present between the dense plasma and the relatively cold cathode body. The production of macroparticles particles is therefore inherently connected to the existence of non-stationary cathode spots.

Numerous studies have been performed to determine macroparticle size and velocity distributions as a function of cathode material and temperature, arc duration and current amplitude, and the presence of external magnetic fields, e.g. [23-26]. The size distributions are wide, from a few nanometers to about the maximum size of craters, i.e. micrometers. Smaller macroparticles are much more frequent than larger once. Materials of low melting point have more and larger macroparticles. Macroparticles move essentially along straight trajectories. The negative charge acquired while moving through plasma plays a role only for the smallest macroparticles.

Magnetically driven cathode spots produce fewer particles, which can be attributed to shorter interaction time of the dense plasma with the cathode material at the spot location. This feature and a better control of the cathode erosion pattern lead to the development of magnetically “steered arcs” [27,28]. Heated cathodes [19] and cathodes of low-melting point material have a high macroparticle erosion rate. This is plausible because the volume of the melted zone between the dense spot plasma and the cathode bulk is relatively large. Most macroparticles are ejected at a shallow angle to the cathode surface, while plasma emission is peaked normal to the surface. A good geometry for a plasma source is one that makes use of this “natural” macroparticle-plasma separation.

Macroparticle filters

Macroparticle filters are structures used to separate and remove macroparticles from the cathodic arc plasma. In most cases, a magnetic field is used to magnetize electrons, allowing an electric field to exist in the plasma. The streaming plasma is guided from the source to the substrate, which is not in line of sight, by a combined magnetic (for electrons) and electric (for ions) mechanism.

Aksenov and coworkers [29] introduced the now-classic 90°-duct filter in the late 1970s. The duct filter consists of a curved duct surrounded by magnetic field coils generating a toroidal field. Baffles are inserted in the duct to reduce macroparticle transport by multiple reflections. This type of filter has been widely used in cathodic arc R&D over the last decades [30-34]. More advanced filters make use of out-of-plane curvature [35,36], and open architecture for better macroparticle removal [37,38]. Filters for larger area coatings are based on a linear design [39], or use the Venetian blind architecture [40,41]. More information on filters can be found in reviews [42,43].

Arcing

Arcing is known as undesirable discharge form on sputter targets. It is nothing else that a cathodic arc; the target is a cathode from a discharge point of view. Arcing can also be observed on negatively biased substrates. It occurs when the local electrical field strength at the substrate exceeds a threshold value of about 10^6-10^7 V/m. The actual value depends on the material, surface conditions, and topography. Even relatively low bias voltage can lead to arcing because most of the voltage drops across a relatively thin sheath. At high surface field strength, emission of electrons can run away and become unstable due to thermal enhancement of the emission. As a result, electron emission can switch into the explosive mode, as it does on an arc cathode. The dense substrate plasma will cause an electric short of the sheath. The substrate voltage “breaks down” to the typical arc voltage level. Substrate arcing can be avoided or at least minimized by using pulsed bias, lower bias voltage, lower plasma density, or a combination thereof. The use of modern bias supplies with fast arc suppression has largely eliminated the problem.

Energetic condensation, subplantation, biasing

Energetic condensation of ions from cathodic arc plasmas is known to lead to dense, well adherent films [33,44]. However, the films can be under high compressive stress, which may

limit thickness before delamination. Stress, hardness, elastic modulus, and other properties need to be carefully considered as function of material system and deposition parameters, especially ion energy and surface temperature.

Energetic condensation is a film growth process from species of hyperthermal energies, giving rise to desorption of loosely bonded adatoms and enhanced surface mobility. Cathodic arc plasma ions have a directed velocity corresponding to a kinetic energy of 19-150 eV, depending on cathode material [21]. This energy is high enough that ions arriving at the substrate surface will penetrate the substrate and come to rest *under* the surface ("*subplantation*" [45]). The kinetic energy of arriving particles is greater than the minimum displacement energy of the material [46] and film growth occurs by deposition of particles under the surface rather than on the surface. Additional to the kinetic energy ions have gained at the cathode spot, ions are accelerated in a thin space charge sheath when the substrate is biased. The average ion kinetic energy can be estimated by

$$E_{kin}(Q) = E_{kin,0} + Q\, e\, V_{sheath}\ , \qquad (1)$$

where Q is the ion charge state number, and V_{sheat} is the voltage drop in the sheath.

Ions bring not only kinetic energy to the substrate but also potential energy [47]. While the kinetic energy (or momentum) is important for the range of sub-surface penetration, the sum of kinetic and potential energy is responsible for substrate heating by ion bombardment. The by far largest contribution to the potential energy is the ionization energy, and therefore the total ion energy at arrival at the substrate surface is approximately

$$E(Q) \approx E_{kin}(Q) + \Sigma\, E_Q\ . \qquad (2)$$

The summation symbol Σ indicates that one needs to add the individual energies of the ionization steps in case of multiply charged ions [47].

Substrate biasing is used to control the sheath voltage and hence the kinetic energy of film-forming ions [48]. Biasing is more effective in cathodic arc plasma deposition compared to other deposition techniques because of the arc plasma's high degree of ionization. Biasing can be applied unipolar or bipolar depending on the effects one whishes to have. For example, when growing an insulating film, pulse bias, or using bipolar pulsing, can reduce surface charging and the risk of substrate arcing. Tailored pulsed bias can also be used to reduce the high compressive stress in the growing film [49].

Reactive deposition

The by far most frequent application of cathodic arc plasma deposition is the reactive deposition of compound films such as CrN, ZrN, TiN, TiAlN, and multilayers thereof. When the compound layer is formed, the metal reacts preferentially with those gases whose energy of compound formation is large, i.e. with the thermodynamically preferred gas species. The plasma may contain contamination such as water vapor, which is typical for high vacuum systems. This issue is especially important for pulsed plasma systems where the water layer on the arc cathode and chamber wall are periodically "scrubbed" by the plasma pulse, and where water vapor is partially ionized. Hydrogen can be incorporated in a film that is supposed to be an oxide or nitride [50]. The incorporation of hydrogen can greatly affect the desired coatings properties such as hardness and elastic modulus [51].

Reactive deposition is commercially done at elevated temperature. One reason is that the deposition process itself heats the substrate. Heating is often utilized to obtain the desired coating texture. A side effect of elevated temperature is the reduction of hydrogen incorporation.

The vast majority of industrial cathodic arc applications do not used macroparticle filters because they would cut down the deposition rate, while macroparticles can be tolerated in many applications. These applications include hard and wear-resistant coatings on cutting and forming tools, decorative and corrosion resistant coatings on doorknobs, faucets, showerheads, and other plumbing and building appliances, and metallic shielding coatings against electromagnetic interference. Specific applications are for example automotive light reflectors and coatings on inside of the plastic housing of cell phones.

Emerging high-tech applications

Macroparticles are a major issue in cathodic arc coatings. For instance, the corrosion resistance is compromised when a macroparticle is incorporated in the coating, disrupting the dense, continuous film. Macroparticles can reduce the shine of a decorative coating. Implementation of macroparticle filters is a possible direction, but reduces deposition rate and increases equipment complexity and cost. Emerging applications in the semiconductor, data storage, and biotechnology areas have stimulated the development of improved filters and other approaches. For example, filtered copper plasma has been used to fill via and trenches of silicon-based computer chips (nano-wiring) [52,53], filtered carbon has been used to form ultrathin protective

layers on magnetic disks and heads [54,55], and cobalt-carbon magnetic nano-composites have been fabricated with filtered arcs [56,57]. Operating the cathodic arc in background gas at elevated pressure, fullerenes and nanoparticles have been produced [58,59]. Current research focuses on emerging applications in the biomedical area, where dense films are sought, for example on medical implants.

Acknowledgements

This work was supported by the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

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