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Magnetron sputtering methods for surface modification of shape memory alloys for applications in orthodontics and endodontics

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SUMMARY

Various magnetron-sputtering methods for surface modification of shape memory alloys (SMA) are described in this paper. These methods belong to the most effective methods, which enable mechanical reinforcing of the SMA, showing numerous advantages over conventional methods of electro-polishing. In addition, surface modified SMA, particularly with equiatomic TiNi coatings, is crucial for further development of various endodontic instruments; wires and brackets used for orthodontic teeth movements. Active coatings with bactericide properties and coatings that can be used as barrier for release of toxic Ni ions from the bulk body of SMA obtained by various magnetron-sputtering methods can be successfully combined. Therefore, the review of these methods is given in this paper, with their main characteristics and drawbacks.

Magnetron sputtering deposition involves surface modification of SMA in a single-layer, multilayer, graded layers, and nanocomposite thin coatings for obtaining systems with superior "functional" characteristics. These are hardness, scratch, abrasion, and erosion resistance, improved adhesion to various technologically important substrate materials such as polymers, hydrophobicity or hydrophilicity, long-term chemical, thermal, and environmental stability, gas and vapor impermeability, and others. This paper is critical review of the advances in the development of magnetron sputtering modified SMA products in dentistry, with in advance predictable physicochemical, structural and antimicrobial properties.

Key words: magnetron sputtering; shape memory alloys; surface modification

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INTRODUCTION

Various magnetron-sputtering methods are developed at industrial level during last several decades [1]. Recent advances particularly in low pressure magnetron sputtering processing have greatly increased the interest for fabrication of various thin films [2]. The main reason for such interest is high extent of the diversity of plasma processes and particularly the coatings on the surface of various materials, including SMA to obtain materials and instruments with superior characteristics [3, 4]. This can be achieved by tailoring energetic interaction between the plasma and the surface, by using bias-controlled or pulsed plasma techniques. In addition, the absence of sharp transition between various interfaces leads to uniform distribution or compensation on internal stresses, in gradient thin coatings, which generally leads to enhanced adhesion and mechanical integrity of such products [5]. Additionally, different substrate shapes can be uniformly coated, including flat, hemispherical, cylindrical shapes, the interior of tubes, etc., with significantly improved mechanical properties in comparison with conventional method of electro polishing. These methods allow deposition of very thin films, with controlled depth, which is essentially important for SMA instruments and tools in orthodontics and endodontics [6]. The objective of the current given paper is to critically review the advances of various magnetron-sputtering processes in obtaining products with desirable properties.

Therefore, several magnetron-sputtering methods are analyzed from the aspect of their mechanisms and potential application in dentistry, as one of the very important area of their further application. Particular attention is paid to films' structure - property relationships, their functional characteristics, and their performance on the SMA substrates, with various details related to the existence of an interphase between SMA and magnetron sputtering coatings and its consequences on the mechanical and other functional properties of so modified surfaces of such alloys.

GENERAL CONSIDERATIONS OF MAGNETRON SPUTTERING METHODS

Magnetron sputtering belongs to physical vapor deposition techniques for producing coatings in vacuum conditions [1]. There are two kinds of these techniques. One

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of them involves thermal evaporation [7], where material is heated in vacuum until its vapor pressure becomes greater than ambient pressure and the second involves ion sputtering during which the high energy ions hit a solid and implant inside of the thin layers of materials, used as target [1, 3]. Previously frequently used method of cathodic sputtering [8] has recently been overcome due to its low rate of deposition and low efficiency. Magnetron sputtering shows numerous advantages compared to other methods due to its high rate of coatings deposition that enables deposition of diverse coatings metal, alloys, or ceramic oxide and non-oxide on the surface of various materials, reaching sometimes the thicknesses up to 5 μm.

BASIC MAGNETRON SPUTTERING MECHANISM

As it is well known, magnetron sputtering is complement method to coatings deposition by other vacuum techniques, like thermal evaporation and electron beam evaporation [1]. Sputtering is the process in which atoms or molecules are ejected from the target surface by bombardment of positive ions, frequently Ar^{2+}. This process must be derived in vacuum or in the conditions of very low pressure, because only in these conditions it is possible to prevent numerous collisions between atoms after their ejection from the target [9]. Therefore, the working pressures of these devices are less than 1 Pa, or 10^{-2} mbar.

As already said, sputtering is the process in which molecules or atoms of target material, during its bombardment with high-energy particles are separated from the material. In magnetron sputtering target is bombarded with positively charged ions generated by the electrical discharge in the gas. During bombardment of the target, the material is separated from it and deposited directly to the substrate. The most important processing parameter is length of the mean free path between two collisions of ions, during magnetron sputtering deposition in vacuum, because it is necessary to maintain high energy ions during the bombardment of the target and prevent collisions of atoms from the target after the separation which leads to poor adhesion to the substrate. The negative side of the process conducted in vacuum is difficulty to get enough ions necessary for the process itself, generated in the plasma state. All cathodic processes are based on the use of plasma that can be obtained using direct current (DC) or radio frequent (RF) methods. Therefore, understanding of conduction of electricity in vacuum is crucial [10]. Figure 1 shows usual relationship between voltage and current intensity of gases at low pressures, where zone H presents conditions required for sputtering. The figure shows the area where the voltage decreases, while current density increases (optimally about 1 mA/cm^2) which leads to ignition. Sources of supply are designed to avoid sparks during sputtering.

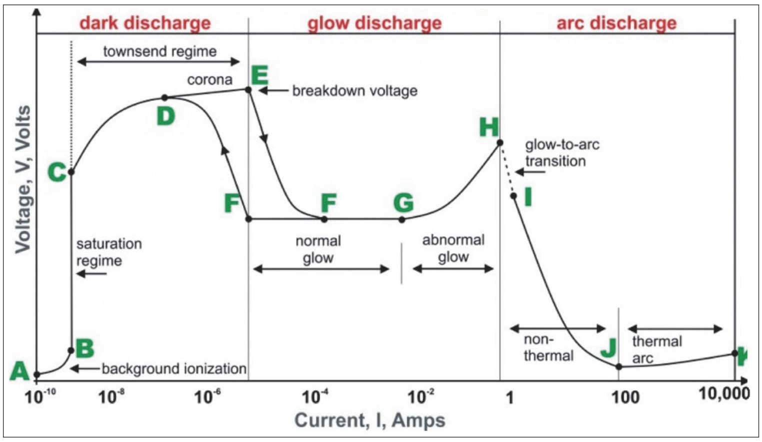

Figure 1. Electric discharge regimes
Slika 1. Režimi električnog pražnjenja

Figure 1 also shows behavior of plasma in gas, with pronounced dark and bright areas expressed at low pressures. In the steady state electrons that came from the cathode, are accelerated towards the positive electrode and ionize the gas molecule. These events are evidenced by the characteristic glow that occurs. Positively charged ions of gas are moving towards the cathode and strike on its surface, leading to formation of secondary electrons (which ionize further gas) and dispersion of new ions. Electrons quickly lose energy due to the collision and voltage and power is concentrated in dark areas. If anode is moved to dark zone, plasma disappears, and sputtering stops. At the lower gas pressure, dark zones increase due to the increase in the mean free path of electrons. Primary electrons can also cross the road to the anode without gas ionization. Therefore, at pressures below 1 Pa, the sputter plasma is extinguished and completely stops. Using more efficient method of ionization, like magnetron sputtering, it is possible to overcome this problem.

The cathode layer begins with the Aston dark space, and ends with the negative glow region [11, 12]. The cathode layer shortens with increased gas pressure. It has a positive space charge and a strong electric field. In Aston dark space, electrons leave the cathode with energy of about 1 eV, which is not enough to ionize or excite atoms, leaving a thin dark layer next to the cathode. In cathode glow, electrons from the cathode eventually attain enough energy to excite atoms. These excited atoms quickly fall back to the ground state, emitting light at a wavelength corresponding to the difference between the energy bands of the atoms. This glow is seen very near the cathode, while on cathode dark space, the electrons from the cathode gain more energy, with tendency to ionize, rather than excite atoms. These excited atoms quickly fall back to ground level emitting light. Subsequently, with the atoms ionizations, the opposite charges have been separated, and do not immediately recombine. As a consequence, more ions and electrons are generated, but no light. This region is sometimes called Crooks dark space, or the *cathode fall*, because the largest voltage drop in the tube occurs in this region. The next area belongs to so-called negative glow, influenced by the strong expressed ionization in the cathode dark space induced by high electron density, with relatively slow rates. Therefore, recombination of electrons with positive ions, leads to intense light, through a process called *bremsstrahlung* radiation. After this area Faraday dark space is present, where electrons keep losing energy, less light is emitted, resulting in another dark space. The anode layer begins with the positive column, and ends at the anode. The anode layer has a negative space charge and a moderate electric field. Positive column is characterized with fewer ions. In this area the electric field increases, resulting in electrons with energy of about 2 eV, which is enough to excite atoms and produce light. With longer glow discharge tubes, the longer space is occupied by a longer positive column, while the cathode layer remains the same. Further increase in electric field results in anode glow, after which is located anode dark space (Figure 2).

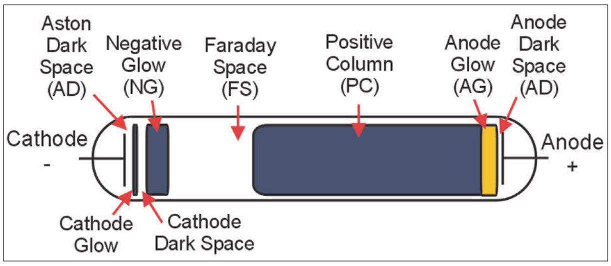

Figure 2. The appearance of different glowing regions that make up glow discharge and their names
Slika 2. Pojava različitih svetlećih regiona koji čine žarište i njihova imena

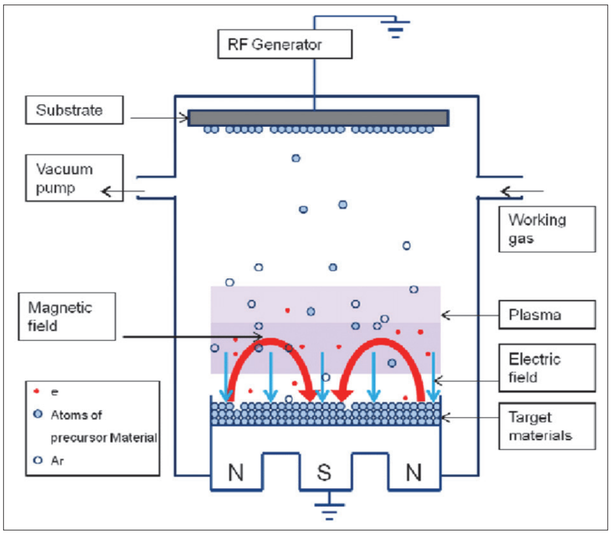

Figure 3. Typical schematic representation of RF magnetron sputtering
Slika 3. Tipični šematski prikaz RF magnetronskog raspršivanja

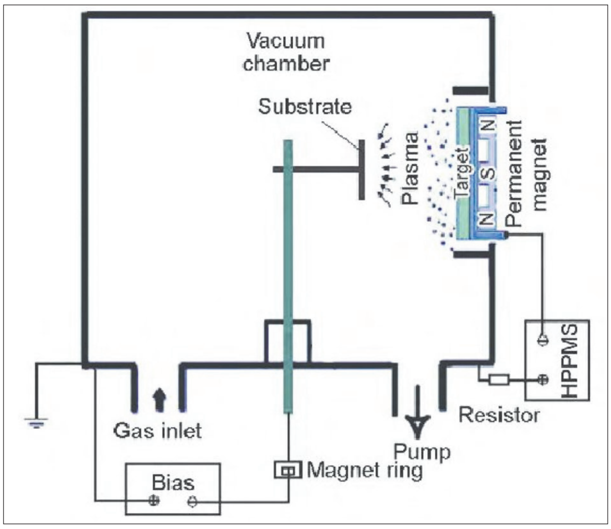

Figure 4. Schematic diagram of the high power pulsed magnetron sputtering (HPPMS) device structure
Slika 4. Šematski prikaz strukture pulsnog magnetronskog raspršivanja (HPPMS) velike snage

TYPICAL CONSTRUCTION OF THE MAGNETRON SPUTTERING EQUIPMENT

Application of the magnetron is based on the use of a magnetic field around the target. The cathode in magnetic field is formed on that way to streamline a magnetic field closed in concentric circles [12]. The essence of the application of such fields is that the primary and secondary electrons arising capture and localize a relatively small area near the cathode, and thus increase the probability of ionizing collisions with the gas atoms and, consequently, increase the efficiency of ionization leading to decrease in impedance of the plasma and the magnetron working at a much lower voltage (500-600 V) than the diode system (several kV).

There are several different types and designs of magnetron but the point is that all of them are based on the physical principle of directing and retaining electrons in a controlled and pre-defined area. Planar magnetron design (schematically shown in Figure 3) is often used because it is very simple and can be made in almost all dimensions and used in continuous processes. Mainly, permanent magnet is used, which geometry is adjusted to obtain suitable magnetic field lines that very close enveloped given target. In order to achieve effective direction and control the electrons, magnetic field must have a minimum strength of 20 mT, but mainly stronger magnetic fields are used.

Several conditions have to be fulfilled in order to successfully design magnetron: cathode must efficiently conduct electricity; due to the inefficiency of the process of obtaining plasma (80% of energy is released through heat), the cathode must have an efficient cooling system; the source of energy must be resistant to pressure differences that arise in the process in a vacuum; good efficiency of targets must be achieved. In the magnetron, plasma is concentrated in front of the target [12]. Therefore, in this area, the strongest bombing is by ionization gas and erosion of the target. The larger is zone where the erosion occurs, the greater is the degree of efficiency, which is very important. Position of maximum erosion constitute an area where B = 0, where the vertical component of the magnetic field is equal to zero, so that the position of the erosion zone can be easily changed and adjusted. In order to achieve the widest possible erosion zone it is necessary to achieve that magnetic lines are nearly parallel to the target, while the field still has the ability to keep electrons. A design that allows this is often very complex and includes more separate magnets (Figure 4).

The thickness of the target is very important because it enables replacement time of target, particularly important for industrial processes. Magnetrons are often used in conditions of constant vacuum, because a frequent replacement and exposure to undesirable oxidation of target is undesirable. In the magnetron design it is essential to ensure strong and effective magnetic field that enables smooth operation. It is very important to ensure the greatest possible uniformity of thickness of the obtained films which directly depends on the pressure under which the processes are carried out, the distance between the substrate and the target material applied, the substrate geometry and its movement, design resources, etc. [13]. The circular magnetron acts as a source of the best film thickness, which can be achieved at a certain distance [14]. The most commonly used magnetrons have the width of the erosion zone ~ 100 mm and the distance between the substrate and the source set in the range of 30-100 mm. Additional uniformity of the film thickness may be achieved by moving substrate or by inserting static or moving mask between source and substrate which retains material and thus increases the uniformity of the thickness through the film geometry.

DC MAGNETRON SPUTTERING

Magnetron sputtering using direct current is simplest and least expensive process of deposition of the given target material on the surface of substrate [3, 15]. In mode DC sputter, target is directly used as a conductor, with the electricity losses given by equation I^2xR (where I is current density and R electrical resistance), and the process can be run with the current ~ 70 W/cm^2 for typical surface of target materials. For sources with a diameter of about 100 mm, the level of power that can be handed over to the plasma is about 5 kW. These conditions enable to obtain the film deposition rates of several microns per minute, which is very useful for continuous industrial processes. Power requirement depends on dimensions of the targets. For larger magnetrons it can reach 50 kW.

Due to the fact that the principle of the magnetron is based on the presence of a magnetic field which is in the front of the target, it is necessary to use very strong magnetic field or thinner targets for magnetic materials. If it is not satisfied, the increase the impedance of the plasma source occurs, and the source has behavior similar to a diode source. The resultant magnetic films are mainly used for the production of storage mediums for computer equipment. Another application of DC spattered films is as coatings on the surface of various materials, like SMA, frequently used in endodontics. For all such films the main request is to achieve as stronger as possible adhesion to the substrate, without defects of the delamination of the coatings.

RF MAGNETRON SPUTTERING

DC magnetron sputtering cannot be applied for targets that act as insulators. The solution of this problem was found in the application of high frequency alternating current. RF magnetron sputtering is developed as a method that allows the use of dielectric material and metals [16]. When the RF power is applied to the target, it must be capacitive paired in that way which enable of developments of the DC potential on its layer. At high frequency, order of the ~ 14 MHz, RF magnetron sputtering shows different behavior and motion of ions and electrons in an alternate field which in turn, means that they cross the various distance in each half-cycles. In the capacitive paired system switching voltage happens, because electrode reacts negatively to compensate the difference of the voltage and creates a negative DC voltage to the cathode surface. Since the capacitive surface electrodes is paired, it can be not only a conductor, bat also insulator such as ceramics and polymers. Due to existence of the DC voltage, the ions bombardments on the substrate surface is carried out, because using this method, the ceramics and glass, or some other isolation materials like polymers can be sputtered.

REACTIVE MAGNETRON SPUTTERING

A large number of dielectric materials that can be sputtered by RF method can be sputtered also by DC magnetron sputtering in the reactive gas atmosphere [17, 18]. As the base of this methods argon gas is used, which is introduced in the reaction chamber together with a small amount of reactive gas. As the reactive gas any gas can be used, if it can react with the target molecules to form a desired product.

Reactive gases are mostly oxygen and nitrogen, but various other gases can be also used. Reaction products are present both on the surface of the magnetron and the substrate, depending on the power source and gas reactivity. The composition of deposited film can be controlled by adjusting the gas flow. Reactive sputter process is cheaper than RF method, due to lower prices of the DC source and target material. The main drawback of this method is saturation of targets. During the increase of gas flow, product of the deposition can be formed at target, which causes reduction of the rate of sputtering and increases the partial pressure of the gas, which leads to further saturation of the target. Very often process inflection point in control loop induce that the process takes place in a very unstable conditions and require exceptional control of process parameters and especially of the gas flow, which requires equipment specially designed for that purpose. The main application of this technique is getting very hard and anti-abrasive films, films for energy purposes, as well as transparent conductive films. Very hard materials such as TiN can be used for endodontic tools, built from SMA, by using sputtering of target in an atmosphere of argon and nitrogen.

PULSE MAGNETRON SPUTTERING

Pulsed magnetron sputtering (PMS) is very efficient plasma method for obtaining nanometric thin films on the surface of various substrates [2, 19, 20], such as SMA frequently used in endodontics for designing endodontic tools, endodontics wires and brackets for teeth (Figure 4). Among numerous parameters that are crucial for satisfied functions of this method, the most important are the pulse frequency, time of application, the working voltage, which enables efficient ignition of the used material as target, providing long-term process stability necessary for the thin layer preparation, significantly improving properties of the SMA, and enhanced level of their application, through reduction of number of defects inside the obtained thin film [20].

It is well known that the microstructure and phase composition of the film directly correlates to the amount of energy that is transferred from the plasma to the film which is formed and which characteristics may be conveniently controlled by adjusting the parameters: ions flux and/ or energy of ions used during target bombardment. In this method, the ratio of ions and neutral particles that bombard the growing film usually is changed by changing the orientation of the substrate toward the ion source [13]. Also flux of negative oxygen ions may be varied by changing the angle of the deposition [21]. Several studies have shown that that the energy deposition during PMS affects not only the density of the film and obtaining very fine film surface, but also enables the obtaining specific phase composition and structure of deposited film in each layer [22].

Applications of this method are numerous and widespread, as the obtaining of the low-emission layers, barrier layers, packages in the food industry, displays, solar cells, solar protection and temperature-sensitive substrates. It is also suitable for the preparation of the layers with higher number of phases. At higher levels of the pulse, this method is very good for the use of alloy targets, as they are SMA used in endodontics [4]. It has been shown that pulse magnetron discharge leads to the same temperature and energy-rich plasma as compared to DC discharge, and the higher energy ions that is deposited to substrate. Based on this, it is clear that the process of PMS provides a number of benefits and allows sputtering by using a broad spectrum of different materials.

MAIN ADVANTAGES OF MAGNETRON SPUTTERING

PMS method enables very good adhesion between the film and the substrate, and its high thickness uniformity [2, 3]. This sputtering method is suitable for obtaining films at low temperatures because the ions which sputter have enough high energy to increase the rate of crystallization [23, 24]. Sputter pulse enables a higher density of plasma, and greater energy of charged particles compared to the DC sputtering. Proper selection of parameter pulse (frequency, duty cycle, operating voltage) ensures working conditions without arcing. Very long-term process stability, reduced density of defects, improved film properties, the increased speed of the dynamic application are essential for good adhesion of the deposited films. TiO_2 or TiN films prepared by magnetron sputtering have been widely used as the dielectric layers, due to its high index of refraction when they are used in multi-layer optical devices [25, 26, 27].

CONCLUSION

Various methods of magnetron sputtering, with all their advantages and drawbacks are given in this paper. The principle of the method, with all functional specificity and main parameters, which can be controlled is described. This method is analyzed as a method of the best choice for the modifications of the SMA used in endodontics and orthodontics. The paper is a base for our further investigations in this area, in the field of the antibacterial coatings and barrier coatings for prevention release of toxic ions contained in SMA, into human body.

APPRECIATION

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Metode magnetronskog raspršivanja za površinsku modifikaciju memorijskih legura za primenu u ortodonciji i endodonciji

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KRATAK SADRŽAJ

U ovom radu su opisane različite metode magnetronskog raspršivanja za površinsku modifikaciju memorijskih legura (*shape memory alloys – SMA*). Ove metode spadaju u najefikasnije metode koje omogućavaju mehaničko ojačavanje SMA, pokazujući brojne prednosti u odnosu na konvencionalne metode elektropoliranja, koje su najčešće korišćene u savremenoj ortodontskoj i endodontskoj praksi. Pored toga, površinski modifikovane SMA, posebno sa ekviatomskim Ti i Ni udelima unutar prevlake, presudne su za dalji razvoj različitih endodontskih instrumenata, žica i konzola koje se koriste za ortodontska pomeranja zuba. Aktivne prevlake sa baktericidnim svojstvima i prevlake koje služe kao barijere protiv otpuštanja toksičnih Ni jona iz SMA unutar organizma mogu biti dobijene različitim metodama magnetronskog raspršivanja, pri čemu se različite varijante ove metode mogu uspešno kombinovati. Zbog svega toga u ovom radu je dat pregled ovih metoda, sa njihovim glavnim karakteristikama i nedostacima.
Magnetronsko nanošenje raspršivanjem uključuje površinsku modifikaciju SMA u jednoslojnim, višeslojnim, gradiranim slojevima i nanokompozitne tanke prevlake za dobijanje sistema sa superiornim „funkcionalnim“ karakteristikama, kao što su vrlo visoka tvrdoća, otpornost na habanje, abraziju i eroziju, poboljšano prijanjanje na različite tehnološki važne supstratne materijale kao što su polimeri, hidrofobnost ili hidrofilnost, dugotrajna hemijska, termička i ekološka stabilnost, nepropusnost gasa i para i drugi. Ovaj rad predstavlja neku vrstu kritičkog pregleda napretka u razvoju magnetronskog raspršivanja modifikovanih SMA proizvoda u stomatologiji, sa unapred predvidljivim fizičko-hemijskim, strukturnim i antimikrobnim osobinama.

Ključne reči: magnetronsko raspršivanje; memorijske legure; modifikacija površine

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UVOD

Različiti postupci magnetronskog raspršivanja razvijeni su na industrijskom nivou tokom poslednjih nekoliko decenija [1]. Novija dostignuća, naročito kod magnetronskog raspršivanja pod niskim pritiskom, uveliko su povećala interesovanje za izradu različitih tankih filmova [2]. Glavni razlog za takvo interesovanje je visok stepen raznovrsnosti plazma procesa i posebno prevlaka na površini različitih materijala, uključujući i SMA, radi dobijanja materijala i instrumenata sa superiornim funkcionalnim karakteristikama [3, 4]. Ovo se može postići prilagođavanjem energetske interakcije između plazme i površine, korišćenjem tehnike kontrole plazme odgovarajućim prednaponom ili primenom pulsirajuće plazme. Pored toga, odsustvo oštrog prelaza između različitih međupovršina dovodi do ravnomerne raspodele ili kompenzacije unutrašnjih naprezanja u gradijentnom sloju tankih filmova / prevlaka, što generalno dovodi do povećane adhezije i mehaničkog integriteta takvih proizvoda [5]. Pored toga, različiti geometrijski oblici podloge mogu biti ravnomerno obloženi, uključujući ravne, polusferične, cilindrične oblike, unutrašnjost cevi itd., sa značajno poboljšanim mehaničkim svojstvima u poređenju sa konvencionalnom metodom elektropoliranja. Ove metode, takođe, omogućavaju deponovanje vrlo tankih filmova, sa kontrolisanom debljinom, što je posebno bitno za SMA instrumente i alate u ortodonciji i endodonciji [6]. Poenta rada je da se kritički sagleda napredak različitih procesa magnetronskog raspršivanja u dobijanju proizvoda sa poželjnim svojstvima.

Stoga se analizira nekoliko metoda magnetronskog raspršivanja sa aspekta njihovih mehanizama i potencijalne primene u stomatologiji, kao jedne od posebno važnih oblasti njihove buduće primene. Pored toga, posebna pažnja posvećena je odnosima strukture i svojstava filmova, njihovim funkcionalnim karakteristikama i njihovim performansama na SMA supstratima, sa bitnim detaljima vezanim za postojanje različitih međufaza između SMA i magnetronskih prevlaka i njihov uticaj na mehaničke i druge funkcionalne karakteristike tako modifikovanih površina ovih legura.

OPŠTA RAZMATRANJA METODA MAGNETRONSKOG RASPRŠIVANJA

Magnetronsko raspršivanje pripada tehnikama fizičkog nanošenja u gasnoj fazi za dobijanje prevlaka u vakuumskim uslovima [1]. Postoje dve vrste ovih tehnika. Jedna od njih uključuje termičko isparavanje [7], gde se materijal zagreva u vakuumu sve dok pritisak pare ne postane veći od pritiska okoline, a drugi uključuje raspršivanje jona tokom kojeg visokoenergetski joni udaraju u čvrsti materijal i ugrađuju se unutar tankih slojeva materijala, koji se koristi kao meta [1, 3]. Ranije korišćena metoda katodnog raspršivanja [8] sada je prevaziđena zbog niske efikasnosti depozicije. Magnetronsko raspršivanje pokazuje brojne prednosti u odnosu na druge metode fizičkog nanošenja u gasnoj fazi, zbog velike brzine nanošenja prevlake i zato što omogućava nanošenje različitih vrsta prevlaka koje mogu biti sačinjene od metala, legura ili keramičkih oksida i neoksida na površinama različitih materijala korišćenih kao substrati, koje dosežu ponekad debljine do 5 μm.

OSNOVNI MEHANIZAM MAGNETRONSKOG RASPRŠIVANJA

Kao što je dobro poznato, magnetronsko raspršivanje je komplementarna metoda za nanošenje prevlaka drugim vakuumskim tehnikama, kao što su termičko isparavanje i isparavanje elektronskim snopom [1]. Raspršivanje je proces u kom se atomi ili molekuli izbacuju sa površine mete bombardovanjem pozitivnim jonima, često Ar^{2+}. Ovaj proces mora biti izveden u vakuumu ili u uslovima vrlo niskog pritiska, jer je samo u ovim uslovima moguće sprečiti brojne sudare između atoma nakon njihovog izbacivanja iz mete [9]. Zbog toga su radni pritisci ovih uređaja manji od 1 Pa, ili 10^{-2} mbar.

Kao što je već rečeno, raspršivanje je proces u kojem se molekuli ili atomi materijala mete tokom bombardovanja česticama visoke energije odvajaju od materijala. U magnetronu je meta bombardovana pozitivno naelektrisanim jonima generisanim električnim pražnjenjem gasa. Tokom bombardovanja mete, materijal se odvaja i nanosi direktno na podlogu. Najvažniji parametar obrade je dužina srednjeg slobodnog puta između dva jonska sudara, tokom deponovanja magnetronskim raspršivanjem u vakuumu, jer je potrebno održavati visokoenergetske jone tokom bombardovanja mete i sprečiti međusobne sudare atoma koji su izbačeni iz mete, što za posledicu ima slabu adheziju takvih jona za podlogu. Negativna strana procesa u vakuumu je vezana za teškoću dobijanja dovoljne količine jona neophodnih za sam proces, koji se nalaze u stanju plazme.

Svi katodni procesi zasnivaju se na upotrebi plazme koja se može dobiti korišćenjem jednosmerne struje (*direct current* – DC) ili radiofrekventne (RF) metode. Stoga je ključno razumevanje provođenja električne energije u vakuumu [10]. Slika 1 prikazuje uobičajeni odnos između intenziteta napona i struje gasova na niskim pritiscima, gde zona H predstavlja uslove potrebne za raspršivanje. Na slici je prikazano područje gde se napon smanjuje, dok se gustina struje povećava (optimalno oko 1 mA/cm^2), što dovodi do paljenja. Izvori jona su dizajnirani tako da se izbegnu varnice tokom raspršivanja.

Slika 1 pokazuje ponašanje plazme u gasu, sa jasno vidljivim tamnim i svetlim područjima, koja su prisutna pri niskim pritiscima. U stabilnom stanju elektroni koji dolaze od katode ubrzavaju se prema pozitivnoj elektrodi i jonizuju molekule gasa. O ovim događajima svedoči karakterističan sjaj koji se javlja. Pozitivno nabijeni joni gasa koji se kreću prema katodi i udaraju na njenu površinu dovode do formiranja sekundarnih elektrona (koji jonizuju dalje gas) i raspršuju nove jone. Elektroni brzo gube energiju usled sudara, pri čemu su napon i snaga koncentrisani u tamnim oblastima. Ako se anoda pomera u tamnu zonu, plazma nestaje, a raspršivanje se zaustavlja. Pri nižem pritisku gasa tamne zone postaju šire zbog povećanja srednjeg slobodnog puta elektrona. Pri tome, primarni elektroni mogu da pređu put do anode a da ne dođe do jonizacije gasa. U skladu sa time, pri pritiscima ispod 1 Pa, plazma raspršivanje se potpuno gasi. Kako se ovi fenomeni javljaju samo na niskim pritiscima, glavni uslov za uspešno raspršivanje je rešavanje ovog problema korišćenjem efikasnije metode jonizacije, kao što je to magnetronsko raspršivanje.

Katodni sloj počinje sa Astonovim tamnim prostorom i završava se negativnim svetlećim područjem [11, 12]. Katodni sloj se skraćuje sa povećanjem pritiska gasa. Karakteriše ga pozitivan prostorni naboj i snažno električno polje. U Astonskom tamnom prostoru elektroni napuštaju katodu sa energijom od oko 1 eV, što nije dovoljno da bi jonizovali ili pobudili atome, usled čega se javlja tanki tamni sloj u blizini katode. U katodnom svetlom prostoru elektroni koji potiču iz katode na kraju postižu dovoljno energije da bi pobudili atome. Ovi pobuđeni atomi se brzo vraćaju u osnovno stanje, emitujući svetlost na talasnoj dužini koja odgovara razlici između energetskih nivoa pobuđenih atoma i njihovog osnovnog stanja. Ovaj sjaj se uočava veoma blizu katode, dok u tamnom prostoru katode elektroni iz katode dobijaju sve više energije, sa tendencijom da dalje jonizuju atome umesto da ih pobuđuju. Pobuđeni atomi, u katodnom svetlom polju, brzo se vraćaju na osnovni nivo i emituju svetlost, dok se nakon toga jonizovani atomi razdvajaju tako da se, iako imaju suprotne naboje, ne rekombinuju odmah. Kao posledica toga, stvara se više jona i elektrona, ali nema svetla. Ovaj region se ponekad naziva Kruksovim tamnim prostorom ili prostorom pada katodnog napona, jer se najveći pad napona u cevi dešava u ovom regionu. Sledeća oblast pripada takozvanom negativnom sjaju, koji nastaje pod uticajem jako izražene jonizacije u tamnom prostoru u okolini katode, koja je indukovana visokom elektronskom gustinom, sa relativno sporim brzinama elektrona. Stoga, rekombinacija elektrona sa pozitivnim jonima dovodi do intenzivne svetlosti, kroz proces koji se naziva zakočno zračenje. Nakon ovog područja prisutan je Faradejev tamni prostor, gde elektroni nastavljaju gubiti energiju, usled čega se emituje manje svetlosti, što rezultira drugim tamnim prostorom. Anodni sloj počinje na granici pozitivno naelektrisanog prostora i završava se na anodi. Anodni sloj ima negativan prostorni naboj i umereno električno polje. Pozitivan anodni prostor karakteriše manji broj jona. U ovoj oblasti se električno polje povećava, što rezultira elektronima sa energijom od oko 2 eV, što je dovoljno da se pobude atomi i proizvede svetlost. Kod dužih cevi za pražnjenje duži prostor zauzima duži pozitivni deo, dok katodni sloj ostaje isti. Dalje povećanje električnog polja dovodi do anodnog sjaja, nakon kog se u delu prostora unutar cevi nalazi tamni anodni prostor (Slika 2).

TIPIČNA KONSTRUKCIJA MAGNETRONSKE OPREME

Primena magnetrona zasniva se na upotrebi magnetnog polja oko mete. Katoda se tada nalazi u magnetnom polju koje se rasprostire u nizu koncentričnih krugova polja oko nje [12]. Suština primene takvih polja je da se primarni i sekundarni elektroni koji nastanu zarobljavaju i lokalizuju u prostoru relativno male površine u blizini katode, i na taj način se povećava verovatnoća jonizujućih sudara sa atomima gasa i, posledično, povećava efikasnost jonizacije, što dovodi do smanjenja impedanse plazme, zbog čega magnetron može da radi na mnogo nižem naponu (500–600 V) od sistema sa diodama (nekoliko kV).

Postoji nekoliko različitih tipova i vrsta dizajna magnetrona, ali poenta je da se svi oni zasnivaju na fizičkom principu usmeravanja i zadržavanja elektrona u kontrolisanoj i unapred definisanoj oblasti. Planarni dizajn magneta (šematski prikazan na Slici 3) često se koristi jer je vrlo jednostavan i može se napraviti u gotovo svim dimenzijama i koristiti u kontinuiranim procesima. Koriste se uglavnom permanentni magneti, čija se geometrija prilagođava da bi se dobio pogodan raspored linija magnetnog polja koje veoma blisko obuhvataju metu. Da bi se postigao efektivan pravac i kontrolisao elektron, magnetno polje mora imati minimalnu snagu od 20 mT, ali se uglavnom koriste jača magnetna polja.

Nekoliko uslova mora biti ispunjeno kako bi se uspešno dizajnirao magnetron: katoda mora efikasno provoditi električnu energiju; zbog neefikasnosti procesa dobijanja plazme (80% energije se oslobađa kroz toplotu) katoda mora imati efikasan sistem hlađenja; izvor energije mora biti otporan na razlike pritiska koje nastaju u procesu u vakuumu; mora se postići dobra efikasnost sudara sa metom. U magnetronu je plazma koncentrisana ispred mete [12]. Zbog toga se u ovom području događa najjače bombardovanje jonizacionim gasom i erozija meta. Što je veća zona u kojoj dolazi do erozije, to je veći stepen efikasnosti, što je veoma važno. Položaj maksimalne erozije predstavlja područje gde je B = 0, odnosno gde je vertikalna komponenta magnetnog polja jednaka nuli, tako da se položaj erozijske zone može lako menjati i prilagođavati. Da bi se postigla najšira moguća eroziona zona, neophodno je postići da su magnetne linije skoro paralelne sa metom, dok polje treba da ima takvu jačinu da još uvek ima sposobnost da zadrži elektrone. Dizajn koji ovo omogućava je često veoma složen i uključuje više odvojenih magneta (Slika 4).

Debljina mete je veoma važna jer ona utiče na vreme zamene mete, što je posebno važno za industrijske procese. Magnetroni se često koriste u uslovima konstantnog vakuuma, jer su česta zamena i izlaganje neželjenoj oksidaciji meta nepoželjni. U dizajnu magnetrona neophodno je osigurati snažno i efikasno magnetno polje koje omogućava nesmetan rad. Veoma je važno da se obezbedi najveća moguća uniformnost debljine dobijenih filmova, koja direktno zavisi od pritiska pod kojim se procesi odvijaju, rastojanja između podloge i primenjenog materijala mete, geometrije supstrata i njegovog načina kretanja itd. [13]. Kružni magnetron deluje kao izvor najuniformnije debljine filma koja se može postići na određenoj udaljenosti od podloge [14]. Najčešće korišćeni magnetroni imaju širinu zone erozije ~ 100 mm i rastojanje između podloge i izvora u rasponu 30–100 mm. Dodatna ujednačenost debljine filma može se postići pomicanjem podloge ili umetanjem statične ili pokretne maske između izvora i podloge, koja zadržava materijal i time povećava uniformnost debljine kroz pogodnu geometriju filma.

DC MAGNETRONSKO RASPRŠIVANJE

Magnetronsko raspršivanje pomoću jednosmerne struje je najjednostavniji i najjeftiniji proces deponovanja datog materijala mete na površinu podloge [3, 15]. U režimu DC raspršivanja meta se direktno koristi kao provodnik, sa gubicima električne energije dobijenim jednačinom $I^2 \times R$ (gde je I gustina struje i R električni otpor), a proces se može izvoditi sa strujom ~ 70 V/cm^2 za tipičnu površinu materijala mete. Za izvore prečnika od oko 100 mm, nivo snage koji se može predati plazmi odgovara naponu od oko 5 kV. Ovi uslovi omogućavaju dobijanje brzine deponovanja filma od nekoliko mikrona u minuti, što je veoma korisno za kontinuirane industrijske procese. Potrebni napon zavisi od dimenzija mete. Za veće magnetrone može dostići 50 kV.

Zbog činjenice da se princip magnetrona zasniva na prisustvu magnetnog polja koje se nalazi u prednjem delu mete, potrebno je koristiti veoma jaka magnetna polja ili tanje mete za magnetne materijale. Ako to nije zadovoljeno, dolazi do povećanja impedanse izvora plazme, a izvor ima slično ponašanje kao kada kao izvor služi dioda. Dobijeni magnetni filmovi se uglavnom koriste za proizvodnju medija za skladištenje kod računarske opreme. Druga primena DC filmova je kao prevlaka na površini različitih materijala, kao što su SMA, koje se često koriste u endodonciji. Za sve takve prevlake/filmove glavni zahtev je da se postigne što jače prijanjanje na podlogu i da se izbegne raslojavanje prevlaka.

RF MAGNETRONSKO RASPRŠIVANJE

DC magnetronsko raspršivanje se ne može primeniti za mete koje deluju kao izolatori. Rešenje ovog problema pronađeno je u primeni visokofrekventne naizmenične struje. RF magnetronsko raspršivanje razvijeno je kao metoda koja omogućava upotrebu dielektričnih materijala i metala [16]. Kada se RF napon primeni na metu, on mora biti kapacitivno uparen tako da omogućava razvoj DC potencijala na površini katode. Na visokoj frekvenciji, reda ~14 MHz, RF magnetronsko raspršivanje pokazuje različito ponašanje i kretanje različitih jona i elektrona u naizmeničnom polju koji, samim tim, prelaze različitu udaljenost u svakom poluciklusu. U kapacitivnom uparenom sistemu dolazi do prekidnog napona, jer elektroda negativno reaguje na kompenzaciju razlike napona i stvara negativni DC napon na površini katode. Pošto su kapacitivne površinske elektrode uparene, kao supstrat može da se koristi ne samo provodnik već i izolatori kao što su keramički materijali i polimeri. Zbog postojanja jednosmernog napona, dolazi do bombardovanja jonima na površini supstrata, tako da ova metoda može da se iskoristi za deponovanje keramike i stakla ili nekih drugih izolacionih materijala poput polimera.

REAKTIVNO MAGNETRONSKO RASPRŠIVANJE

Veliki broj dielektričnih materijala koji se mogu raspršivati RF metodom može se raspršiti i DC magnetronskim raspršivanjem u atmosferi reaktivnog gasa [17, 18]. Kao noseći gas kod ove metode koristi se argon, koji se uvodi u reakcionu komoru zajedno sa malom količinom reaktivnog gasa. Kao reaktivni gas može se koristiti bilo koji gas, ako može da reaguje sa molekulima mete da bi se formirao željeni proizvod.

Reaktivni gasovi su uglavnom kiseonik i azot, ali se mogu koristiti i razni drugi gasovi. Produkti reakcije su prisutni i na površini magnetrona i na podlozi, u zavisnosti od karakteristika izvora energije i reaktivnosti gasa. Sastav deponovanog filma kontroliše se podešavanjem protoka gasa. Proces reaktivnog raspršivanja je jeftinijii od RF metode, zbog nižih cena izvora jednosmerne struje i materijala mete. Glavni nedostatak ove metode je zasićenje meta. U toku povećanja protoka gasa, proizvod deponovanja se formira na meti, što dovodi do smanjenja brzine raspršivanja i povećanja parcijalnog pritiska gasa, a to izaziva dalje zasićenje mete. Vrlo često proces inflektivne tačke u kontrolnoj petlji dovodi do toga da se proces odvija u veoma nestabilnim uslovima i zahteva izuzetnu kontrolu procesnih parametara, a posebno protoka gasa, što zahteva opremu posebno projektovanu za tu svrhu. Glavna primena ove tehnike je dobijanje veoma tvrdih i antiabrazivnih filmova, filmova za energetske svrhe, kao i prozirnih provodnih filmova. Visoko abrazivni materijali, kao što je TiN, mogu se koristiti za endodontske alate izgrađene od SMA korišćenjem raspršivanja jona mete u atmosferi argona i azota.

PULSNO MAGNETRONSKO RASPRŠIVANJE

Pulsno magnetronsko raspršivanje (*pulsed magnetron sputtering* – PMS) veoma je efikasna plazma metoda za dobijanje nanometarskih tankih filmova na površini različitih podloga [2, 19, 20], kao što su SMA, koje se često koriste u endodonciji za dizajniranje endodontskih alata, endodontskih žica i nosača za zube (Slika 4). Među brojnim parametrima koji su od ključnog značaja za zadovoljenje funkcija ove metode, najznačajnije su frekvencija pulsa, vreme primene, radni napon, koji omogućava efikasno paljenje materijala korišćenog kao mete, osiguravajući dugoročnu stabilnost procesa potrebnu za pripremu tankih slojeva, značajno poboljšavajući svojstva SMA i nivo njihove primene kroz smanjenje broja defekata unutar dobijenog tankog filma [20].

Dobro je poznato da mikrostruktura i fazni sastav filma direktno koreliraju sa količinom energije koja se prenosi iz plazme u film koji se formira, iz čega sledi da se karakteristike tankih filmova/prevlaka mogu pogodno kontrolisati podešavanjem parametara: fluks jona i/ili energija jona korišćenih tokom bombardovanja mete. U ovoj metodi se odnos jona i neutralnih čestica koje bombarduju rastući film obično menja promenom orijentacije supstrata prema izvorima jona [13]. Takođe, fluks negativnih jona kiseonika može varirati promenom ugla deponovanja [21]. Nekoliko studija je pokazalo da energije deponovanja tokom PMS-a ne utiču samo na gustinu filma i dobijanje veoma fine površine filma već omogućavaju i dobijanje specifičnog faznog sastava i strukture nanetog filma u svakom sloju [22].

Primena ove metode je brojna i široko rasprostranjena: dobijanje slojeva niske emisije, barijernih slojeva, specifičnih pakovanja u prehrambenoj industriji, displeja, solarnih ćelija, zaštitnih prevlaka od sunca i podloga osetljivih na promenu temperature. Takođe je pogodna za pripremu slojeva sa većim brojem faza. Na višim nivoima pulsa, ova metoda je veoma dobra za upotrebu meta-legura, kao što su SMA koji se koriste u endodonciji [4]. Pokazano je da pulsno magnetronsko pražnjenje dovodi do iste temperature i plazme bogate energijom kao i DC pražnjenje, pri čemu se visokoenergetski joni deponuju na podlogu. Na osnovu svega navedenog, jasno je da PMS proces pruža brojne prednosti i omogućava raspršivanje na brojnim različitim vrstama materijala.

GLAVNE PREDNOSTI MAGNETRONSKOG RASPRŠIVANJA

PMS metoda omogućava veoma dobru adheziju između filma i podloge i visoku uniformnost debljine [2, 3]. Ova metoda raspršivanja je pogodna za dobijanje filmova na niskim temperaturama, jer joni koji se raspršuju imaju dovoljno veliku energiju za povećanje brzine kristalizacije [23, 24]. Pulsni impuls omogućava veću gustinu plazme i veću energiju nabijenih čestica u odnosu na DC raspršivanje. Pravilnim odabirom parametarskog impulsa (frekvencija, radni ciklus, radni napon) osiguravaju se radni uslovi bez iskrenja. Veoma dugotrajna stabilnost procesa, smanjena gustina defekata, poboljšana svojstva filma, povećana brzina dinamičke primene neophodne su za dobru adheziju deponovanih filmova. TiO_2 ili TiN filmovi pripremljeni magnetronskim raspršivanjem široko se koriste kao dielektrični slojevi zbog visokog indeksa loma kada se koriste u višeslojnim optičkim uređajima [25, 26, 27].

ZAKLJUČAK

U radu su prikazane različite metode magnetronskog raspršivanja, sa svim njihovim prednostima i nedostacima. Opisan je princip metode, sa svim funkcionalnim specifičnostima i glavnim parametrima koji se mogu kontrolisati. Ova metoda se analizira kao metoda najboljeg izbora za modifikacije SMA koje se koriste u endodonciji i ortodonciji. Rad je osnova za naša dalja istraživanja u ovoj oblasti, u oblasti antibakterijskih prevlaka i barijernih prevlaka za sprečavanje oslobađanja toksičnih jona sadržanih u SMA u ljudsko telo.

ZAHVALNOST

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