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Laser Induced Plasma of Titanium (Ti) as a Source of Thin Film Deposition on Mg-alloy used in Biomedical Implants

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Abstract

Laser induced plasma is a promising tool for generation of ions, electrons, neutrals as well as excited species with vast range of applications in material processing, improving electrical, optical, and mechanical properties as well as oxidation resistance of many materials. Magnesium alloys are widely used in biomedicine and industrial applications. The significant effects of laser fluence and nature of background gases (Ar,O_2) on sputtering yield, structural modifications, and on mechanical properties of laser irradiated Mg-alloy have been discussed. The sputtering yield of laser induced plasma of mg-alloy has been calculated by using piezoelectric effect principle-based device, i.e. Quartz Crystal Microbalance (QCM). X-Ray Diffraction analysis (XRD) has been performed to confirm the oxide formation of laser treated samples in O_2 environment. The Vickers Micro-hardness testing reveals that hardness of laser irradiated Mg-alloy is increased by increasing fluence in both environments as compared to untreated sample. Mg-alloy being biocompatible, are widely used in biomedical implant. But due to rapid corrosion and high degradation rate, it is desirable to change its properties by coating Ti layer on it. The thin films deposition, based on laser ablation called pulsed laser deposition (PLD) can be used to modify the material characteristics like hardness, conductivity, corrosion resistance and bio compatibility. The properties of surgical magnesium alloy can be improved by pulsed laser deposition of titanium (Ti) in different ambient environments.

Keywords: Laser Induced Plasma, Quartz Crystal Microbalance (QCM), Pulsed Laser Deposition (PLD)

Introduction

Laser ablation of solid targets in the presence of different background gasses corresponds to the enhancement of energy coupling to the lattice, offers confinement and gas dynamical effects, is highly beneficial in laser assisted ablation, deposition, and plasma formation [1]. In laser induced plasma, after shooting a focused beam on to the target material, photon energy is transformed into electronic excitation, chemical and thermal mechanical energy of high density, high temperature plasma consisted of neutrals, ions, electrons as well as excited species. The reactive or inert nature, of ambient environment being important controlling factor, plays an extensive role in the evolution and expansion of plasma plume, and becomes more complex as compared to vacuum. The various significant physical processes such as gas dynamics, shielding effect, formation of shock waves, clustering, and the interaction of the plume with an ambient environment, are important in numerous applications of pulsed laser-deposition, ion implantation, and micro/nano-structuring of materials [2, 3]. The controlling parameters of laser (pulse duration, number of laser pulses, pulse energy, wavelength) as well as the parameters of irradiated material (bonds strength, chemical composition, work function, melting point etc) are responsible for energy and dose of ions generated by plasma. The calculated sputtered amount of laser ablated target material will be help full in different applications such as thin film deposition, ion implantation as well as micro/nano structuring of materials [3]. The Time-of-Flight mass spectroscopy (TOF), Faraday Cup (FC) and Quartz Crystal Microbalance (QCM), are some frequently using techniques for sputtering yield measurement [4]. The QCM is a mass sensitive instrument, with significant applications in surface science, working on the principle of piezoelectric effect [4] to monitor the small mass changes as well as thin films areal density of target material. Mg-alloys are widely used in biomedicine and industry and various physical properties such as hardness, conductivity, corrosion resistance and bio compatibility can be improved after laser treatment. Khalfaoui et al., reported the changes of laser surface treatment of Mg-alloy ZE41, and their results revealed an increase in micro hardness and corrosion resistance of laser treated samples. Magnesium is a light metal with a density of 1.74 g/cm^3 , comparable to the density of human bone (1.75 g/ cm^3), mostly used in bone implant [5, 6]. Also due to their superior mechanical compatibility, biocompatibility and degradability, magnesium and magnesium alloys have a wide range of biomedical uses. Magnesium is one of the body's macronutrients, involved in several metabolic activities that promotes calcium deposition, which is good for bone formation. So far, available magnesium and magnesium alloys as well as newly developed magnesium alloys all show a high degradation rate and rapid corrosion, which is problem in bone implant. The mostly used biomaterials in human body, are stainless steels, Co-based alloys and Ti-based alloys, used in various medical applications of orthopaedic, dental and cardiovascular. Mostly stainless steels and Co-based are avoided due to major biological drawback of corrosion, and other is release of toxic ions of Ni and Cr into bodily fluids. Recently, Ti alloys are getting much attention because of excellent biocompatibility, good mechanical properties, decent corrosion resistance [7]. The respective shortcomings of titanium and magnesium materials limit their widespread use. The disadvantage of titanium is that its Young's modulus (E), although lower than that of other metals, is still somewhat different from that of human bone, which certainly leads to "stress shielding". In this paper author will discuss the effect of ambient environment and laser fluence on mechanical properties of Mg-alloy (AZ91D), with prospective experiments of pulsed laser deposition of Ti on Mg-alloy. The thin films deposition, on the surface of a bulk material with different configuration such as anticorrosion coatings on metal alloys, ion implantation of metals and their alloys by magnetron sputtering or by faraday cup and most interesting is based on laser ablation called pulsed laser deposition (PLD) are used to modify the material characteristics like hardness, conductivity, corrosion resistance and bio compatibility. The properties of surgical magnesium alloy can be improved by pulsed laser deposition of titanium (Ti) in different experimental conditions such as type of laser, laser parameters, and nature of ambient environments.

Materials and Methods

The squared (25 mm x 25 mm x 7 mm) shaped Mg-alloy AZ91D (Mg 90 %, Al 9 %, Zn 0.1 %) samples (Alpha Eiser), after mechanically polishing, grinded and ultrasonically cleaned for 15 min, were mounted on the rotatable sample holder and were placed in a stainless-steel vacuum chamber. The Nd: YAG laser source of wavelength of 532 nm and pulse duration of 6 ns was used to irradiate the target material. The laser focused spot size area on irradiated samples of Mg-alloy measured by SEM images was 4.3 × 10^3 cm^2. The Quartz Crystal Microbalance (QCM 200 Quartz Crystal Microbalance Digital Controller, SRS. Inc. USA) used to measure the sputtering yield, by exposing Mg- alloy to 100 laser pulses at eight different fluences of 11.6, 16.3, 20.9, 25.6, 30.3, 34.9, 39.6 and 44.2 J/cm^2 under two different environmental gasses of Ar and O_2 filled at pressure of 10 Torr. Experimental diagram, figure 1 showing that incident laser beam after passing through the focusing lens hits the target material at 45° angle to ablate the target material, that is going to deposit on the quartz crystal placed parallel to the target surface. For the compositional analysis of the laser irradiated Mg-alloy samples, X′ Pert PRO(MPD) X-ray diffractometer was used. The Vickers hardness test was employed, to study the surface micro-hardness analysis of laser irradiated Mg-alloy as a function of laser fluence in different ambient environments.

For pulsed laser deposition, there will be a slight difference in experimental setup, that we will consider, such as by using femtosecond laser source, the target material will be Ti, and instead of using quartz crystal of QCM, a substrate of Mg-alloy will be used to deposit the layer of Ti on it.

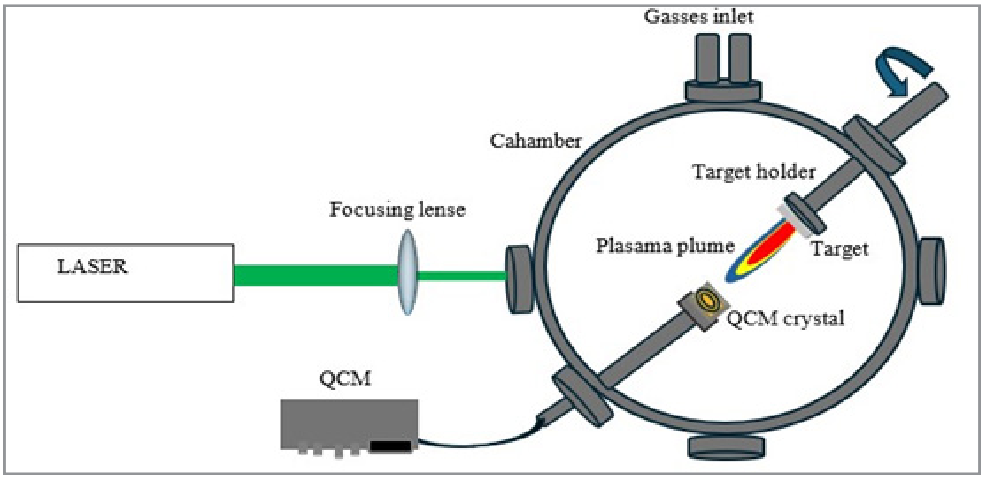

Figure 1: Schematic diagram of experimental setup for calculation of sputtered mass of laser induced plasma of Mg-alloy

Analysis

The deposited mass of laser irradiated Mg-alloy on the quartz crystal is measured by using Sauerbrey equation.

$$\Delta f = C_f \Delta m \qquad (1)$$

where Δf is the change in frequency of the quartz crystal because of ablated mass, deposited on quartz crystal, Δm is the amount of deposited mass, the calibration constant C_f value is 56.6 Hzμ g^{-1} $cm2$ for 5 MHz At-cut quartz crystal. The sputtering yield Y of laser irradiated Mg-alloy is calculated by using equation 3.

$$Y = 2\pi r^2 \int_0^{\pi/2} D(\theta) sin\,(\theta) d\theta \qquad (2)$$

$$= 2\pi r^2 \frac{D(\theta)}{n+1} \qquad (3)$$

here D (θ) is the area density along a direction with the angle θ of the deposited material with respect to the surface normal. As QCM is placed parallel to the target material, therefore, the value of cosnθ is considered 1 [8]. In QCM the mass deposited on the quartz crystal is measured in cm^{-2}, so the value of D (0) is mass deposited on the crystal. In equation 3 the value of n=3. The deposition rate depends upon the beam spot size and increases with increasing focused spot area. By Kool' s analysis, the value of angular distribution should not be greater than 3 for beam diameter. The value of laser spot for 100 pulses in our case is 0.89 mm which is less than the reported value of Kool so by putting value of n=3 we can measure the sputtering yield of ablated target [9].

Results and Discussion

The sputtering yield of laser ablated Mg-alloy as a function of laser fluence, under both environments of inert (Ar) and reactive (O_2) gasses filled at pressure of 10 Torr, is measured by QCM as shown in graph of figure 2. Initially an increasing trend, from 14.48×10^{14} to 23.49×10^{14} (atoms/pulse) and from 4.5×10^{14} to 22.60×10^{14} (Atoms/pulse) by increasing fluence from 11.6–34.9 J/cm2 was observed due to more energy deposition under ambient environments of Ar and O_2 respectively. After that with the further increase in fluence till up to maximum of 44.2 J/cm2, decrease in the sputtering yield of 19.78×10^{14} and 19.94×10^{14} (atoms/pulse) is observed . As an effect of background environment, overall, the sputtering yield values are higher in Ar environment as compared to O_2 environment. These graphs reveal that the laser fluence and nature of ambient environment are the key parameter for controlling sputtering yield of Mg-alloy.

The highly intense laser pulse, hit the target material to heat the target surface up to tens of thousands kelvin temperature, and results into the formation of plasma plume consists of neutrals, ions electrons as well as excited species [10, 11]. The reactive or inert nature, of ambient environment plays a substantial role for the evolution and expansion of laser induced plasma, becomes more complex in the presence of ambient gas environment as compared to vacuum. Multi-Photon Ionization (MPI) and Inverse Bremsstrahlung Ionization (IBI) are governing mechanism for ionization and excitation of investigated material results into generation and growth of high density, high temperature plasma. Initially by increasing laser fluence, both processes of MPI and IBI are increased due to more energy deposition and correspondingly sputtering yield is increased [11].The insignificant decrease in sputtering yield, after achieving the maxima is due to the self-regulating regime or saturation, which correspond to less energy deposition to the target surface. The plasma shock front absorbs the incoming electromagnetic radiations (laser supported detonation), the energy absorbed by the plume is balanced by energy losses and no significant increase in sputtering yield is observed [12].

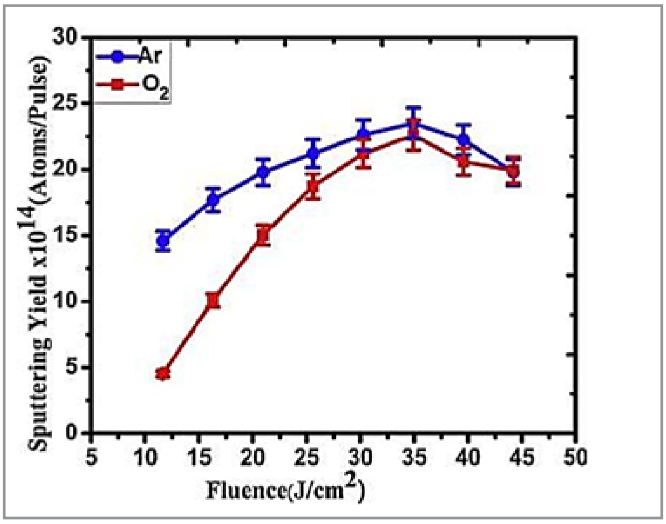

Figure 2: Sputtering yield measurements of laser induced plasma of mg-alloy as a function of laser fluence under ambient gasses of Ar and O_2 filled at pressure of 10 torr

Figure 3 represents XRD pattern of laser irradiated Mg-alloy with various diffraction peaks at the fluence of 25.6 Jcm^{-2} under 10 Torr pressure of Ar and O_2. The diffraction peak identified at 32.18˚ correspond to (100) plane of Mg [Reference code: (01-089-4894)]. Whereas diffraction peaks observed at 36.113˚, 38.140˚, 64.940˚ correspond to (411), (420) and (721) planes of $Mg_{17}Al_{12}$ [Reference code: (01-073-1148)].

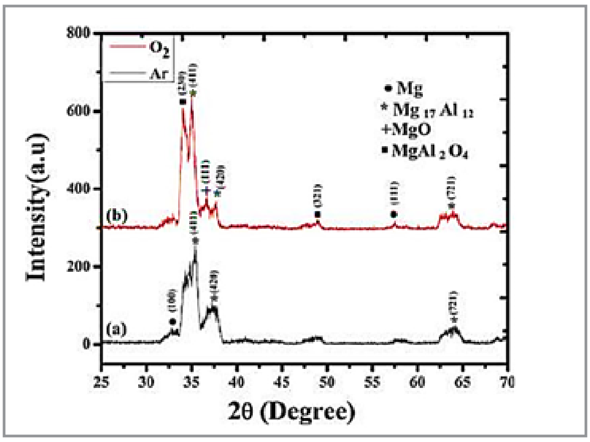

Figure 3: XRD patterns of laser irradiated Mg-alloy at the fluence of 25.6 J/cm2 under different ambient environments of (a) Ar and (b) O_2 filled at fixed pressure 10 torr

The peak identified in spectra of laser irradiated target material in Ar environment are same as reported by Jin et al. [13] for untreated Mg-alloy. For irradiated Mg-alloy in O_2 environment [14], due to oxide formation new peak of MgO (111) has been identified at 36.944˚. The other diffraction peaks identified at 33.995˚ and 36.944˚ correspond to (230) and (111) plane of $MgAl_2O_4$ [Reference code:(00-047-0254)] and MgO [Reference code: (01-089-7746)]. The slight peak shifting and increase in peak intensity for all laser-treated samples, can be attributed to the growth of compressive stresses and surface defects generated after laser irradiation of the target material. When Laser beam hit the target surface, correspond to the heating of target material and on cooling different processes such as resoldification and recrystallization take place. The gas atoms are diffused along the grain boundaries and therefore, result into the increase in peak intensity [1].

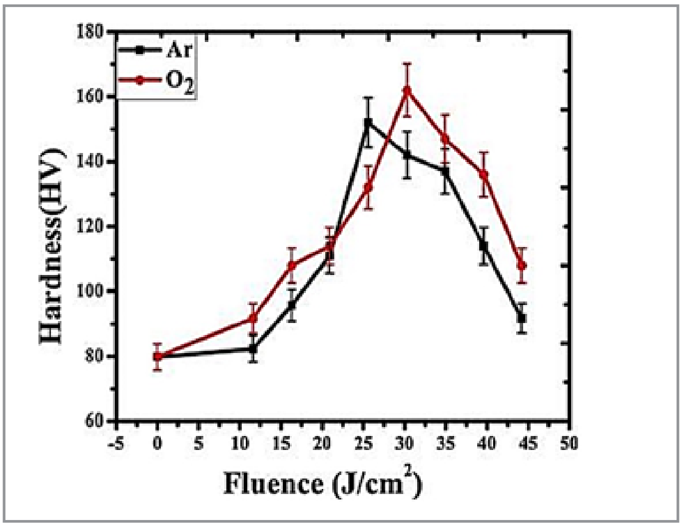

Figure 4: The comparison of micro-hardness of untreated and laser treated Mg-alloy in different environmental gasses of Ar and O_2 filled at fixed

The variation in micro hardness of laser ablated Mg-alloy in ambient environment of Ar and O_2 as a function of laser fluences ranging from 11.6–44.2 J/cm^2 is shown in figure 4. The overall the value micro-hardness of laser treated samples is increased at laser fluences, in both environments as compared to untreated sample having value of micro-hardness is 79.8 HV. So, we can have a clue that after laser treatment of Mg, the mechanical properties are enhanced as compared to untreated samples. The graph of figure 4, shows that by increasing fluence from 11.6–30.3 J/cm2 , the hardness increases from 82.3–142 HV and from 80 to 162 HV under ambient environment of Ar and O_2 respectively. Afterwards, it decreases up to 92 and 108 HV by further increasing fluence up to maximum of 44.2 J/cm^2. However, due to oxide formation in O_2 environment the micro-hardness of laser ablated Mg-alloy is greater in case of ambient environment of O_2 as compared to Ar. The variation in values of micro-hardness can be attributed to lattice disorder of the material [1]. These changes are produced due to thermal compressive stresses and structure modifications due to the laser induced heating. The results of micro-hardness are well correlated with both sputtering yield and XRD analyses. The maximum value of sputtering yield is responsible for maximum surface and mechanical modification in both environments.

Conclusion

The various physical properties such as hardness, conductivity, corrosion resistance and bio compatibility can be improved after laser treatment of any target material. Consequently, for any material, there is suitable combination of laser fluence and environmental conditions, which correspond to efficient increase in sputtering yield as well as change in structural and mechanical properties of laser irradiated material. These suitable parameters can make the materials more useful for different applications of thin film deposition, ion implantation, surface structuring, material processing, and in industry. Mg-alloy being biodegradable are widely used in biomedicine and automobile industry due to high strength. Magnesium alloy is designed to be an absorbable bone implant. For bone implant applications, the bone healing duration is about one year or longer. Therefore, it is desired that the bone implant provides strong support during the first 3 months and then it gradually degrades in volume and strength in the following healing process. So far, available magnesium and magnesium alloys as well as newly developed magnesium alloys all show a high degradation rate in a biological environment. As due to its bio compatibility used in bone fixation but still have some obstacles such as rapid corrosion, initial healing stage. The objective of next work is to improve the behaviour of surgical magnesium alloy by titanium ion implantation

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