Al-Nahrain Journal for Engineering Sciences **NJES** 28(3)347-350, 2025
http://doi.org/10.29194/NJES.28030347

Enhancing Emission Intensity of Spectral Lines Ti I Using Nanoparticle enhanced laser-induced breakdown spectroscopy (NELIBS)

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Paper History:

Received: 31st Jul. 2024

Revised: 26th Nov. 2024

Accepted: 20th Jan. 2025

Abstract

Enhanced signal emission from nano (ESEN) coated titanium target over than that from normal untreated one was investigated. Four samples of Ti alloy were adjusted, the first sample was left untreated, the second and third samples were coated with plasma sputter at thicknesses of 35nm and 70nm, and the last sample was treated with a drop of colloidal Au nanoparticle solution prepared by laser ablation. The (ESEN) was monitored with Ti at 413.7 and 393.3 nm. It was obtained that the spectral emission from the nano-laser ablation had a greater improvement than that from the plasma sputter coating or bulk target. Enhancement factors were found up to ten folds, and show the spectroscopic line induced patterns by laser energies (100,150, and 200mJ) from the alloy with and without gold.

Keywords: LIBS, Gold Nanoparticles, NELIBS, Laser Ablation, Plasma, Plasma Sputter Coating.

تعزيز شدة انبعاث الخطوط الطيفية Ti I باستخدام NELIBS

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الخلاصة:

تم التحقيق في انبعاث إشارة معززة من هدف التيتانيوم المطلي بالنانو (ESEN) أكثر من الهدف العادي غير المعالج. تم تعديل أربع عينات من سبيكة Ti، وتركت العينة الأولى دون معالجة، وتم طلاء العينتين الثانية والثالثة بالرش البلازمي بسمك ٣٥ نانومتر و٧٠ نانومتر، وتم معالجة العينة الأخيرة بقطرة من محلول جسيمات نانوية غروانية من الذهب تم تحضيرها بواسطة الاستئصال بالليزر. تمت مراقبة (ESEN) باستخدام Ti عند ٤١٣,٧ و٣٩٣,٣ نانومتر. وقد تبين أن الانبعاث الطيفي من الاستئصال بالليزر النانوي كان له تحسن أكبر من ذلك الناتج عن طلاء الرش البلازمي أو الهدف السائب. تم العثور على عوامل تعزيز تصل إلى عشرة أضعاف، وتظهر أنماط الخطوط الطيفية المستحثة بواسطة طاقات الليزر (١٠٠ و١٥٠ و٢٠٠ مللي جول) من السبائك مع الذهب وبدونه.

الكلمات المفتاحية: LIBS، جسيمات النانو الذهبية النانوية، NELIBS، الاستئصال بالليزر، البلازما، طلاء الرش البلازمي.

1. Introduction

Nanoparticle enhanced laser-induced breakdown spectroscopy (NELIBS) has recently gained attractiveness due to its capacity to increase signal background ratio compared to conventional LIBS [1], [2]. This procedure can be achieved by integrating a metal thin film or by drying a drop of colloidal solution containing metal nanoparticles on the surface (NPs) [3], [4]. In addition, the benefits of this process include its simplicity, controlling the size and concentration of NPs and the fact that, following examination, the laser irradiation eliminates the NPs, leaving a clean surface. As suggested by Dell'Aglio et al [5] signal enhancement can be attributed to the growing deposition of laser intensity from sample thanks to the plasmonic coupling the NPs with applied laser beam. This coupling affects both early plasma start from the sample surface and decreases the plasma ignition threshold. Hattori et al. [6] may have pioneered the use of nanoparticles for LIBS signal enhancement in 2009; they applied colloidal particles to the leaf surface for emission enhancement, with emphasis on the effect of the size and material of the metallic particles. After that, the majority of NELIBS studies focused on utilizing metal nanoparticles (gold, silver, platinum, and copper) ensuring plasmon resonance in the optical spectrum. The use of these NPs is justified by their high absorption cross section for optical light. Some studies have examined the influence of concentration, size, shape and also utilizing nanomaterial as a target on plasma properties and emission intensity [7–9] Kiris, has compared the efficiency of signal intensity when used Ni-C NPs and Ag-Cu in the ranges from UV and visible [10].

Despite the large number of works devoted to NELIBS, the factors providing analytical signal improvement cannot be considered fully defined. The purpose of this work is to observe the effect of gold NPs deposited at Ti alloy surface on intensity for different lines.

2. Experimental

Nanoparticles (Gold) have been prepared by laser ablation at liquid phase (PLAL) technique utilizing Nd: YAG at (1064 nm), and (800 mJ), and frequency (1 Hz). As shown in Fig.1, gold metal plate disk ablated with (500) pulse in deionized water. A drop of yielded solution was then deposited on Ti-6Al-4V alloy with dimension (1×1 cm) and thickness (1.1 mm).

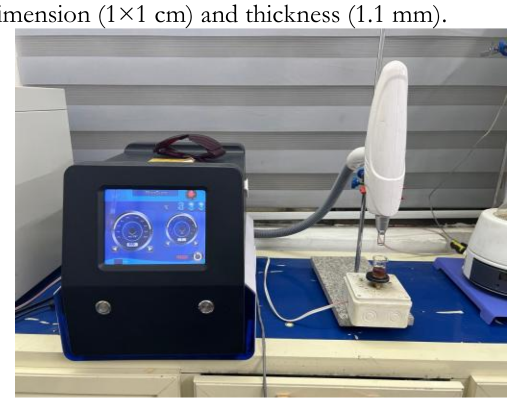


Figure (1): The experimental setup used for (PLAL) method.

On the other hand, the Au films were deposited on Ti alloy using plasma sputter coating shown in Fig. 2 at two different sputtering time of 34.3 sec and 68.6 sec respectively. The thickness of obtained films (D) can be calculated based on sputtering current (I), sputtering time (T) and material constant (K) in the following formula [11]:

$$D = K.I.T \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The evaluated values of film thickness (D) were 35nm and 70 nm respectively.

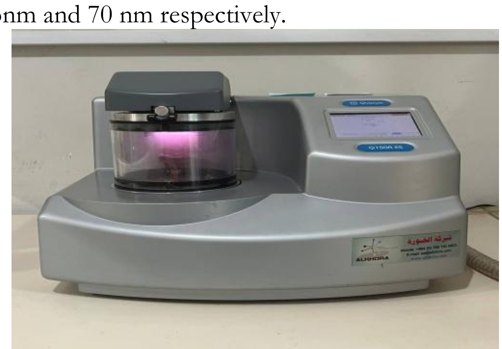


Figure (2): Plasma sputter coating.

LIBS set up[12], [13] has been used to produce plasma by Nd: YAG laser (1064 nm), pulse energy was 100 to 200 mJ. Emission linens were recognized using optical spectrometer. Optical fiber cable was used to collected plasma light.

Recognition of involved lines were matched with NIST database [14]. Table 1 listed the examined four samples, first sample of Ti-6Al-4V alloy was kept untreated, second and third samples were deposited using plasma sputter coating at thicknesses of 35nm and 70nm, and finally, last sample of Ti alloy treated with a drop of colloidal Au solution of nanoparticles.

Table (1): The examined samples used in this study.

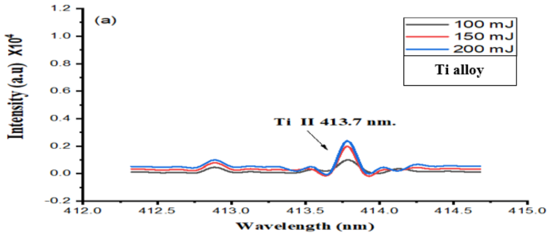
No.	samples	Preparation methods
1	Ti alloy	Uncoated Ti alloy.
2	Ti alloy	Ti with coating 35 nm gold by plasma sputter coating
3	Ti alloy	Ti with coating 70 nm gold by plasma sputter coating
4	Ti alloy	a drop of colloidal Au solution - Ti alloy

3. Results:

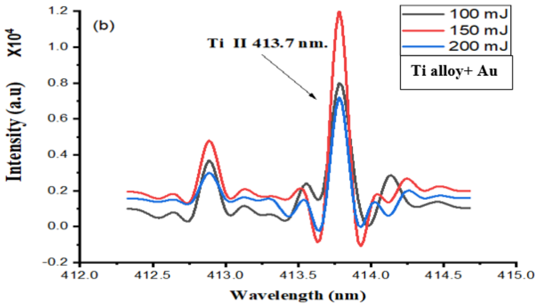
To investigate the influence of attaching an Au layer on intensity, we examined the LIBS obtained on coated Ti alloy samples and uncoated. Fig. 3 shows the emission lines generated by laser energies 100,150, and 200mJ. As can be seen, the lines intensity increases with increasing the energy due to ablated substance. Following the de-excitation process, these ablated and excited atoms operate as generators of further photons. However, the increase in line intensity with rising laser energy is not the same for all lines, and can be attributed to variations in plasma temperature (Te), and create variations in electronic distributions for levels of energy, illustrated by the Boltzmann as show in Fig. 3a. [15][16].

However, as compared to untreated alloys, the lines were more intense and distinct in coated Ti alloys containing Au nanoparticles for all three laser energies as illustrated in Fig. 3b. These curves show common trend and agreement with other pioneering works [17]. The fundamental distinction between LIBS and NELIBS is the variety of ablation processes generated by the presence NPs and their interaction with the laser. Shifting energy distribution has influence on plasma creation and its subsequent characteristics, as well as plasma emission [18]. Also, the probability of breakdown will be high when the target coated with nanoparticles as they facilitate heat transfer to the target surface [19,20].

As it can be seen in the set of graphs in Fig. 4, in the presence of Au nanoparticles, line intensity has increased by increasing laser energy, firstly at energy 100mJ the intensity increased by 0.8, while intensity became 1.2 at 150 mJ, as well as the intensity increased by 0.76 at 200 mJ.



(a)



(b)

Figure (3): Spectra for Ti alloy target at different laser energies: a)for Ti without gold , b)for Ti with nano-gold.

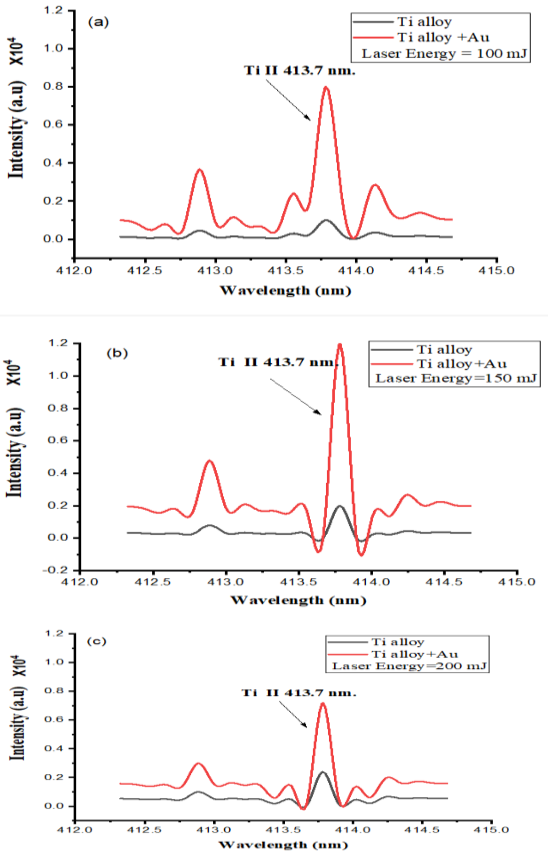


Figure (4): Comparison of line intensity of Ti alloy with and without Au nanoparticles at different energy.

Finally, the difference between the emission lines can be clarified in Fig. 5 by considering spectral signals of Ti I (394.5) nm under different preparing conditions at fixed laser energy. We can easily notice that the spectral lines of titanium have increased significantly when using a drop solution containing gold nanoparticles compared to depositing a layer of gold film using plasma sputtering. However, the signal increases with the increase in the thickness of the deposited gold layer. The significant enhancement of emission lines arises from a combination of plasmonic field enhancement, energy transfer mechanisms, interfacial optical effects, and changes in surface chemistry and morphology due to the presence of Au nanostructures on Ti alloys. These effects synergistically boost the intensity and sharpness of the emission lines, making them significantly more prominent.

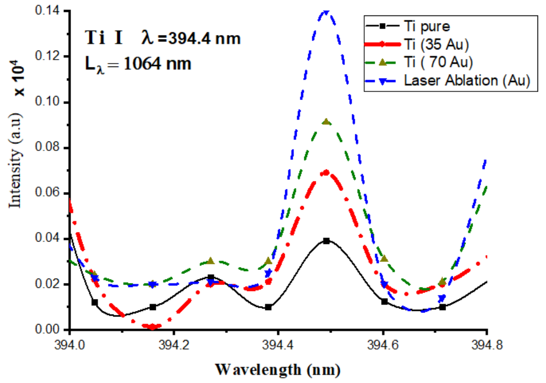


Figure (5): Comparison between with different Nano particles methods.

Further, distinction of enhancement factor (the ratio of the intensities of NLIBS/ LIBS) for 413.7 and 393.4 nm lines is given in Fig.6 a & b. One may note that the enhancement factor has decreased with the laser energy for both spectral lines. The highest enhancement factor of 413.7 nm line is 8.5 at 100 mJ and reduces exponentially till a value of 1.0 at 400 mJ. Likewise, enhancement factor of the of 393.4 nm line is 10.1 at the lowest laser energy. Also, it has decreases exponentially till reaching 2.0 at 400 mJ.

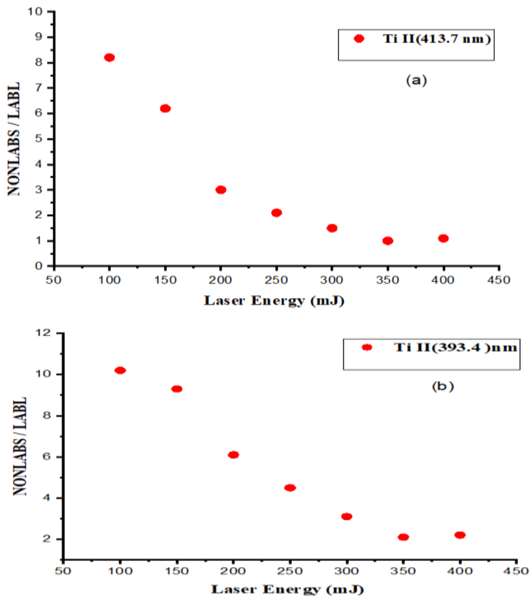


Figure (6): enhancement factor of Ti I lines (a)413.7nm, (b) 393.4 nm.

4. Conclusions

LIBS spectra of Ti alloys with Au NPs and without Au coated its surface have been considered to observe the effect of NPs on the intensity of different spectral lines of the laser induced plasma. Four samples were prepared: the first Ti alloy sample was left untreated, the second and third samples were coated with plasma sputter at thicknesses of 35nm and 70nm, and the last sample was treated with a drop of colloidal Au nanoparticle solution prepared by laser ablation at liquid phase. The lines intensity increases with increasing the energy due to an increase ablated substance. Being compared to untreated alloys, the lines were more intense and distinct in coated Ti alloys containing Au nanoparticles for all three laser energies. Signal enhancement has been qualified by considering enhancement ratio; however, this ratio has decreased exponentially with increase the laser energy.

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