Application of the nitrogen laser to microspectral analysis of a substance

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Received May 16, 2008

The experimental research on development of the express methods of control and analysis of nano-dimensional protective coatings with the help of the compact and simple nitrogen laser are described. Due to the focused laser radiation on the investigated surface, the laser plasma in material vapor of a given sample appears. Experimental results of the spectral analysis of a laser plasma luminescence of various materials are presented.

Introduction

At present the development of the methods of express control and different materials composition diagnostics is one of the topical problems. Spectral methods are widely used for its solution. These methods are usually based on molecules and atoms excitation with the help of an electric discharge either arc, spark, or Grimms ones. X-ray fluorescent spectroscopy is also used.

Recent investigations have revealed that intensive laser radiation can also be used for spectral analysis.[1–4] In reality pulse-periodic CO_2 lasers as well as neodymium and excimer lasers are used for the solution of these tasks.

The effect of laser radiation is based on the phenomenon of laser plasma ignition under its influence on the surface of the investigated material. This plasma radiates specific lines of molecules and atoms the material contains. The advantage of laser plasma compared to the electric discharge one is the possibility of its ignition both on the metal and on dielectric. Besides, the laser helps us to increase significantly the efficiency of diagnostics. The main difficulty in laser spectral analysis is the presence of continuous spectrum in laser plasma glow which increase threshold material composition detection. The authors of Ref. 5 showed that at low ambient gas pressure the laser plasma is composed of two parts: primary and secondary plasma. Primary plasma appears in the first moments after the influence initiation radiating mostly continuous spectrum while in secondary plasma mostly the material atoms radiate. The division of spectrum registration according to the time allows us to decrease the influence of continuous background in the investigated sample.

Usually laser plasma spectral analysis is conducted with the help of neodymium laser. However, it was shown in Ref. 4 that the use of UV lasers laser plasma is preferable regarding the increase of signal-noise ratio and plasma glow stability. Among the UV lasers N_2 laser is the most easy to use and the cheapest one compared to excimer lasers.

This article presents the results of experimental research on express methods of nano-dimensional protective coatings composition analysis and control with the help of a simple and compact nitrogen laser.

Equipment and experimental results

In our experiments we used transverse discharge nitrogen laser designed in HCEI SB RAS (Fig. 1).

Fig. 1. Nitrogen laser exterior view.

Laser dimensions are $60 \times 42 \times 23$ cm, the mass is 23 kg. Laser radiation had the following characteristics: 4×14 mm beam size, 1.5 mJ pulse energy, 4–6 ns radiation pulse duration, up to 100 Hz pulse repetition rate. The laser operated on either pure nitrogen (at 120 torr pressure) or on N_2 and He gas mix (at 1.25 atm pressure). The working gas was pumped by a diametrical fan installed in laser working chamber.

Block scheme of the experimental setup is illustrated in Fig. 2.

0235-6880/08/08 637-03 $02.00

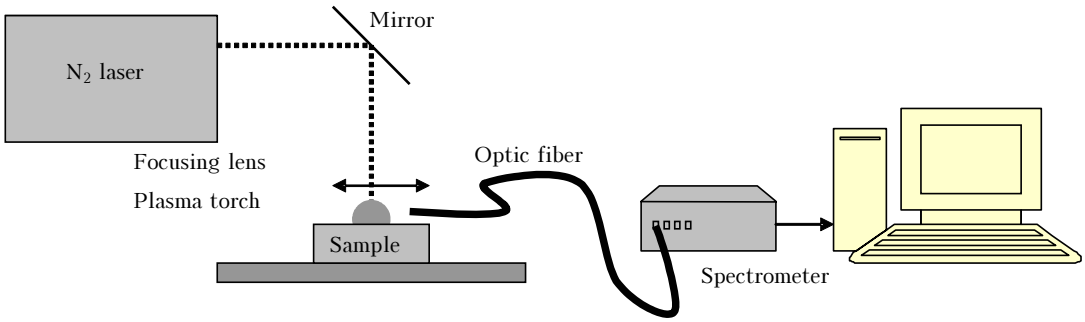


Fig. 2.

Being turned with a mirror the laser radiation was focused on the target by a lens with $F = 60$ mm focal distance. "Klavi" spectrometer or HR-4000 spectrometer produced by "Ocean Optics" and having 0.25 nm resolution were used for spectrum registration. The registered radiation from laser plasma was input into the spectrometer by means of optic fiber. The information on radiation spectral composition was processed on a PC with the help of a special program.

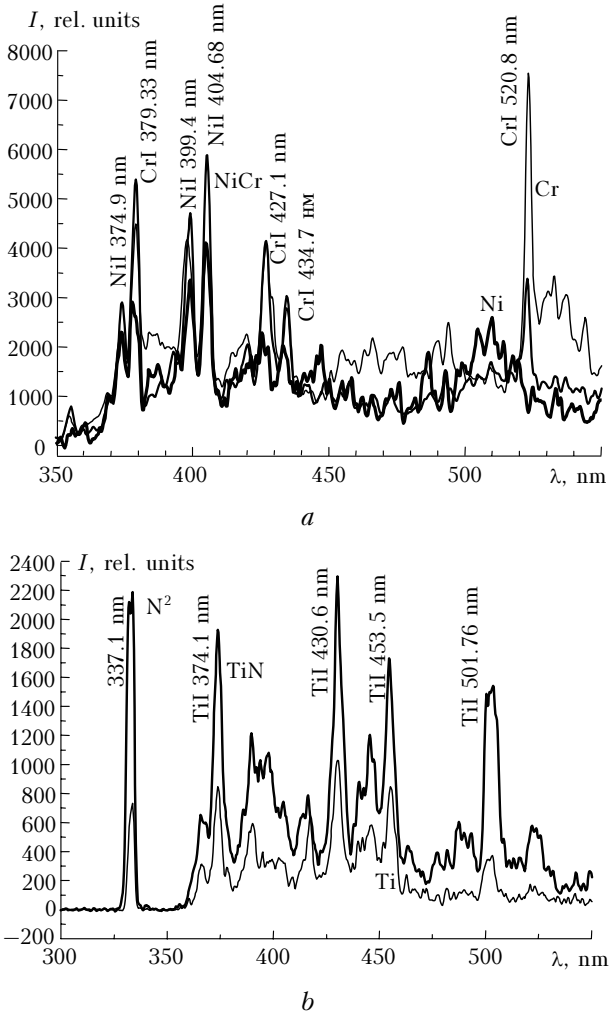


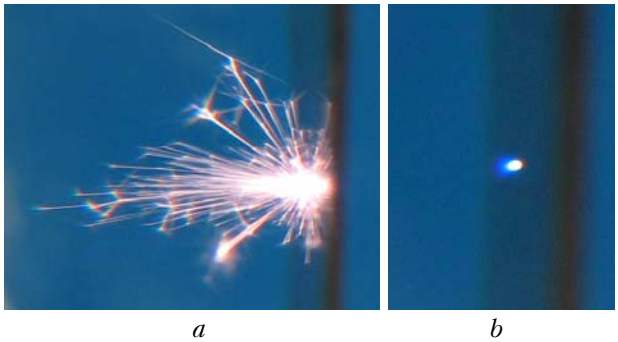
Fig. 3. Laser plasma glow spectrum on the surface of NiCr alloy and pure elements Ni, Cr, Ti (*a*) and on the surface of TiN (*b*) coating.

We chose such elements contained in any protective coating as titan, nickel, copper, and chrome as the most interesting ones for the analysis. The intensities of spectral lines received at laser lamp radiation on the coating surface made of nickel and chrome alloy and pure Ni and Cr are illustrated in Fig. 3*a*.

We can see that plasma spectral lines correspond only to the transitions of the excited atoms while there are no transitions on ions.

The intensities of spectral lines received at laser lamp radiation on the coating surface made of titanium nitride are illustrated in Fig. 3*b*. We can see the lines of titan and dispersed radiation of nitrogen laser on 337.1 nm operational wavelength. The presence of intensive spectral lines for the investigated elements allows us to identify it accurately and to master the methods of coating elemental composition determination. In all the cases we can see only the lines of the excited atoms, though bright plasma is observed.

Figure 4 illustrates the photographs of plasma glow on the surface of titanium nitrate coating (Fig. 4*a*) and steel substrate (12X18H10T) (Fig. 4*b*). The intensity of the beam falling on the target was identical in both cases.



a *b*

Fig. 4. Plasma glow on the surface of titanium nitrate coating (*a*) and substrate material 12X18H10T (*b*).

We observed a significant difference in the glow which as we assume is caused by the presence of inner stress of hard coating (titanium nitrate) crystal lattice. After numerous impacts of the radiation in one point the spark character of the glow disappeared.

Figure 5 illustrates the change of plasma glow intensity with time in the presence (see Fig. 4*a*) and in the absence of sparks (see Fig. 4*b*).

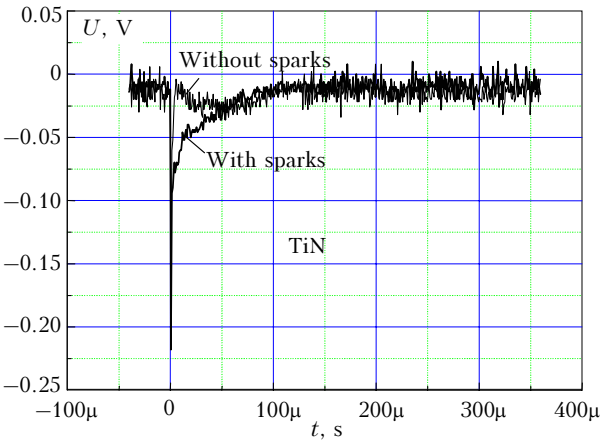


Fig. 5. The change of plasma glow (see Fig. 4) intensity with time in the presence and in the absence of sparks.

It can be seen that in the absence of sparks there is a short emission at radiation pulse while in the presence of sparks the duration of radiation pulse intensity is longer. As we assume this prolongation is caused by the movement and the glow of big particles of covering material.

The focusing of laser radiation to a small size allows us to conduct a thorough investigation of composite alloys homogeneity which is of principle importance for the solution of specific tasks. For example, for the purposes of hydrogen power engineering one needs to create a thin and extremely homogenous YZr-film on the surface of the porous material. In order to accomplish this task one needs a homogenous YZr-alloy. Figure 6 illustrates the investigation results of YZr-cathode homogeneity.

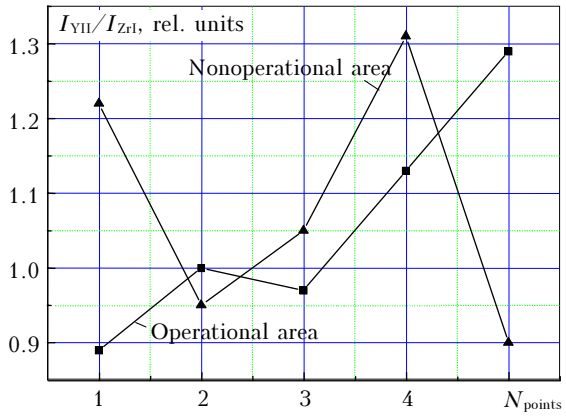


Fig. 6. The relation of YII ions radiation intensity at $\lambda = 4374.9$ Å to the intensity of Zr atoms glow at $\lambda = 4710.1$ Å. The material operational area was used in an installation designed for thin films saturation.

The relation of Y(II) ions radiation intensity at $\lambda = 4374.9$ Å wavelength to Zr atoms glow intensity at $\lambda = 4710.1$ Å was chosen as a measured parameter due to its strongest spectral lines. The size of the laser spot on the surface of the investigated sample was equal to 0.2×2 mm. As we can see from Fig. 6 the measured relation changes from point to point in the range of 50% not depending on the fact whether an investigated area was operational or not. We can assume that the measuring of Y and Zr concentrations occurs in the same or a greater range. Such homogeneity is not sufficient enough for the creation of the required coatings.

As the N_2 laser operated in pulse-periodic mode one could define the moment when the protective coating is completely removed and spectral lines of substrate material substitute the lines of coating material. It could be done by controlling laser plasma spectral composition in each pulse. If we find the coating thickness carried away during a single pulse then we could use this method for the determination of thickness of the film of such coating.

In order to work out this method we conducted some experiments on pulse removing of the protective coatings made of titanium nitrate and having different thickness. The most important thing was to choose the optimal radiation intensity on the surface of the coating. In our experiments it varied from 10^7 to $3 \cdot 10^9$ W/cm^2. This intensity was obtained in a focal spot of 50–200 μm diameter. Efficient removal of the material was observed at maximum intensities. The change of coating thickness from 30 nm to 10 μm practically did not influence the quantity of the material removed per one pulse. As a result we found out that at 2 GW/cm^2 radiation intensity in one pulse a 20 nm thick layer of TiN surface is removed. It allowed us to remove 60 nm layer at 3 pulses and 1 μm layer at 50 pulses.

Conclusion

Thus, the use of a simple nitrogen laser has great capabilities for the determination of elemental composition and homogeneity of the material in air at atmospheric pressure as well as for an efficient determination of 100–1000 nm coatings composition and thickness. The results of our experiments can be used for the development of control express methods not only for the studied materials but also for any other.

Acknowledgements

The work was financially supported by RFBR (Project No. 08-02-90029).

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