STUDY OF UV LASER ABLATION OF NITRIDED STEELS USING INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

Viktor KANICKY[a,*], Jan MUSIL[b], Marcel BENDA[c] and Jean-Michel MERMET[d]

[a] *Department of Analytical Chemistry, Masaryk University, 611 37 Brno, Czech Republic; e-mail: viktork@chemi.muni.cz*

[b] *Skoda Research Ltd., Tylova 47, 316 00 Plzen, Czech Republic*

[c] *Department of Physics, University of West Bohemia, 306 14 Plzen, Czech Republic; e-mail: benda@kfy.zcu.cz*

[d] *Laboratoire des Sciences Analytiques, Universite Claude Bernard Lyon I, Bat. 308, 696 22 Villeurbanne Cedex, France*

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A depth profile study of nitrided steels containing Ti or V sputtered in the surface layer was performed by means of laser ablation inductively coupled plasma atomic emission spectrometry. An Nd:YAG laser was used in the Q-switched mode and operated at 355 and 266 nm. The laser ablation patterns were obtained on the material surface by moving the ablation cell relative to the laser beam by means of an XY-translator. Depth resolution was obtained by using successive limited numbers of ablation cycles. The corresponding transient signals of Ti or V and Fe were measured simultaneously with a dual monochromator. The effect of the number of cycles, the laser power and laser wavelength on the time-dependent behaviour of the Ti or V and Fe line intensities was studied along with the erosion rate. It was found that the erosion rate was lower than 0.6 μm per cycle and depended on the depth of penetration. Emission of sputtered Ti and V was mainly observed in an external layer of less than 2 μm. The laser wavelength did not modify the shape of the crater but significantly changed the line intensity of Fe. The Fe line intensity was also enhanced during the ablation of the nitrided steel compared with the ablation of untreated steel. This study contributes to the knowledge of behaviour of the modified metal surface during interaction with the laser radiation, which is important for development of the method for determination of composition of nitrided surface layers.

Key words: Atomic emission spectrometry; Inductively coupled plasma; UV laser ablation; Depth profile; Nitrided steel.

Laser ablation inductively coupled plasma (LA-ICP) spectrometry is currently used for the bulk analysis of various types of solid materials[1]. Laser ablation can be used for any type of materials, in particular for those difficult to dissolve. It has been recently demonstrated that laser ablation can also be used for analysis of a material deposited on

* The work was performed while on leave from Masaryk University.

a substrate[2]. A 3 μm ZrTiN coating on high speed steel was analyzed with a cycle-by-cycle laser ablation. The erosion rate was found to be 0.1 μm per cycle using an Nd:YAG laser at 355 nm. Ceramic coatings or modified surface layers present an interesting challenge for laser ablation. The physical properties of these layers can be significantly different from those of the bulk material and, therefore, the erosion rate can be different and difficult to control. Moreover, as for any direct solid analysis, and particularly for heterogeneous material, a lack of standards can be a severe limitation for quantitative analysis. Use of internal standardization could overcome this limitation. When powder is used, internal standard can be added with a binding agent before pelleting[3,4]. Internal standard can also be included in samples which are fused to form glass beads[4,5]. However, if a multilayer material has to be analyzed, an internal standard should be present in both the layer and the substrate. However, this procedure cannot be used when the material surface is modified by a physical or chemical treatment. It is known that the surface layer of metal which is modified by oxidation (e.g. atmospheric) exhibits different behaviour in comparison with deeper layers when interacting with laser beam[6]. This is also the case of nitrided steels.

Nitridation of steels is used to improve the hardness, the corrosion resistance and the coefficent of friction of the surface of the material. Plasma nitriding process is carried out in a mixture of 1 : 1 $N_2 + H_2$ at a substrate temperature of 550 °C and a pressure of 1 kPa (ref.[7]). Transition elements form intersticial nitrides, where atoms of nitrogen occupy gaps in crystal lattices of the metals. During the nitriding process, elements such as Ti or V can be evaporated and sputtered in the nitrided layer to enhance the formation of compounds with high hardness. These nitrides have a metallic appearance, are chemically inert, exhibit a high hardness, and have a high melting point. Hardness for TiN and VN is improved by a factor of 1.6–1.9 compared with the untreated steel and the melting point is 2 950 and 2 180 °C, respectively. It should be noted that the stoichiometry of the nitrides is not necessarily observed as there can be a lack of nitrogen. The interaction with the substrate during the nitriding process was expected to be up to 20 μm (ref.[7]). Because of the above-mentioned difference in the physical properties, it can be, therefore, expected that the process involved in the ablation of nitride layer would be different from that of untreated steel. The aim of this work was, therefore, to use laser ablation ICP atomic emission spectrometry (AES) for the study of the erosion rate of both nitrided steels and untreated steels and the spatial distribution of Ti or V in the nitrided layers.

EXPERIMENTAL

A pulsed Nd:YAG laser (Surelite Laser, Continuum, Santa Clara, CA) was used for ablation. It was decided to use a UV wavelength to minimize the penetration of the laser beam into the material and to promote the ablation layer by layer. The low energy obtained in the UV was no disadvantage as a soft ablation was thought to be preferable. Therefore, the Q-switched laser was operated at 355 and 266 nm with a 10 Hz repetition rate and a 4–6 ns pulse width. The energy per shot was in the 0.8–2 mJ range

and 1–5 mJ range at 266 and 355 nm, respectively. The laser beam was focused on the target surface using a fused silica plano-convex singlet lens. A power density of about $7 \cdot 10^9$ W/cm^2 was estimated from the experimental crater diameter (about 250 μm), the pulse width and the pulse energy. The average laser power was measured with an Astral TM Laser Power/Energy Meter, Model AD 30 (Scientech, Inc., Boulder, CO).

The ablation cell consisted of a sample holder, a glass cylindrical chamber (ca 140 cm^3) with a silica optical window and a cell support. The laser beam was perpendicular to the target surface. The useful diameter of the sample was 14 mm. The silica window was angled at 10° to eliminate back reflections within the focusing lens. Two argon gas flow rates were used: a 100 cm^3/min flow rate to sweep out the ablated material from the target surface and to minimize the aerosol deposition on the chamber walls, and a 0.5 dm^3/min flow rate to transport the ablated material to the ICP. Mass flow controllers (Brooks 5850 TR/5878 series) were used for both flows. The ablated material was transported along 3 m of polyamide tube to the ICP. The inner diameter of the tube was 4 mm. Computer-controlled, motor-driven XY translation stages (model PCC 2/4, Schneeberger, Linear Technology, Bretigny-sur-Orge, France) allowed the ablation cell to be moved with respect to the laser beam. A speed of 1 mm/s was used for a polygonal trajectory pattern. The length of one cycle of this pattern was 14.4 mm and its cycle duration was 14.80 s.

The ICP instrument was a Spectroflame Model D from Spectro Analytical Instruments that consisted of a 0.75 m dual monochromator, allowing the simultaneous measurement of two lines. The V II 309.311 nm and the Fe II 259.940 nm lines were measured simultaneously, whereas the Ti II 334.941 nm line was measured sequentially with a delay of 5 s. Using solutions, it was verified that no spectral interferences occurred. An integration time of 0.5 s was used. The 27.12 MHz generator was operated at a forward power of 1.4 kW and at an plasma and intermediate argon flow rates of 15 and 1.0 dm^3/min, respectively. Two argon flow rates were used with the ablation cell: a 0.1 dm^3/min flow rate to take up the ablated material from the surface material and a 0.5 dm^3/min to transport the ablated material to the ICP along 3 m of polyamide tube.

The use of a single cycle or two successive cycles led to a transient signal. Peak area was used for the determination of the intensity. Then the ablation cell, the tube and the torch were flushed with argon for 2–3 min and the ablation cycles were repeated[2]. In some instances, a multicycle ablation (40 cycles) was used.

A Form Talysurf Series profilemeter (Rank Taylor Hobson) was used for the determination of the crater depth[2].

Two samples of nitrided steel and one sample of untreated steel were studied. One sample was nitrided with simultaneous sputtering of Ti, the other with V. The steel contained (wt.%): 0.85% C, 4.20% Cr, 0.45% Mn, 5.00% Mo, 0.035% P, 0.035% S, 0.45% Si, 1.85% V, 6.25% W.

RESULTS AND DISCUSSION

Erosion Rate

Regardless of the laser wavelength and up to a number of cycles of 40, the diameter of the crater was found to be in the 200–250 μm range. The erosion rate was found in the interval of 0.1–0.2 μm per cycle for the untreated steel and 0.13–0.6 μm per cycle for the nitrided steel (Table I). The erosion rate was dependent on the number of cycles, the laser energy and the laser wavelength.

In any instance, the highest erosion rate was observed for the first cycle, followed by a decrease over a 1–5 cycle range (Table I). For Ti sputtered nitrided steels, the erosion rate was higher than 0.4 μm per cycle for the first cycle whereas the mean erosion rate was less than 0.15 μm per cycle over a 40-cycle range (Table I). Such a change was also observed for untreated steels but to a lower extent. Note that a 0.1 μm per cycle erosion rate was found for ZrN or TiN coating on high speed steel[2] at 355 nm and for 5 mJ. These results are significantly different from those found for glass ablation[8,9]. In this case, a constant erosion rate of 18 μm per cycle was found at 355 nm and 5 mJ up to a depth of about 2 mm.

A slight increase in the erosion rate was observed with increasing energy. For a 4-cycle experiment performed at 355 nm on Ti sputtered nitrided steel, the mean erosion rate was increased from 0.2 to 0.3 μm per cycle. However, there was no major advantage to use a high energy as a degradation of the depth resolution was obtained.

It seemed that the use of the 266 nm wavelength was beneficial for the erosion rate. For untreated steel, a similar erosion rate was obtained at 266 and 355 nm (Table I)

TABLE I
Effect of ablation conditions[a] on erosion of steel

Sample	*E*, mJ	λ, nm	*n*	*d* total, μm	*d* per cycle, μm
u	0.8	266	5	1.0	0.20
u	2	355	4	0.6–0.8	0.15–0.20
u	2	355	40	4.2–5.0	0.11–0.13
n-Ti	1	355	1	0.4–0.6	0.40–0.60
n-Ti	1	355	3	0.8–1.0	0.26–0.33
n-Ti	1	355	4	0.8	0.20
n-Ti	2	355	4	0.8	0.20
n-Ti	3	355	4	1.0	0.25
n-Ti	5	355	4	1.2	0.30
n-Ti	5	355	10	2.2	0.22
n-Ti	2	355	40	5.0–6.0	0.13–0.15
n-V	0.8	266	1	0.4	0.40
n-V	0.8	266	5	1.0	0.20
n-V	2	266	1	0.6	0.60
n-V	2	266	5	1.3	0.26

[a] *E* laser energy, λ laser wavelength, *n* number of cycles, *d* crater depth. [b] Steel: u untreated, n nitrided with sputtered Ti (n-Ti) or V (n-V).

although the laser energy used at 266 nm was half of that used at 355 nm. However, there was no significant difference for nitrided steels.

Depth Resolution

A multicycle continuous ablation (41 cycles, 355 nm, 2 mJ) indicated (Fig. 1) that Ti could only be observed during the first cycles, i.e. within a layer of less than 2 μm. The results were compared with those obtained for untreated steel. As mentioned in Table I, the crater depth was 5 μm. The peak intensity of the transient signals was obtained for the first cycles in the case of the nitrided steel. This could be expected for Ti but not for Fe as the percentage of Fe was decreased in the nitrided layer compared with that of the untreated steel. In the case of the untreated steel, the Fe response was rather flat and the maximum signal was not observed during the first cycles. As the same intensity scale was used for both samples, it may be seen (Fig. 1) that the Fe line intensity was far higher for the nitrided steel than for the untreated steel, although the ablation could be expected to be less efficient because of the higher hardness. However, the blackness of the surface was more pronounced for nitrided steel than for untreated steel, which might result in a more efficient laser beam absorption. Even when the substrate was reached, there was a significant difference of a factor of 2.5 between the two Fe steady signals. As the erosion rate was similar for both samples, i.e. an average of 0.2 and 0.14 μm per cycle for nitrided and untreated steels, respectively (Table I), the erosion rate could not be used to explain the difference in the signal intensities. A possible explanation could be related to a different size of the ablated particles, resulting in a different transport efficiency and a modified evaporation and atomization rate in the ICP. This problem would require additional experiments to be solved.

Because the Ti signal was observed only during the first cycles, it was thought necessary to improve the depth resolution. This is why a cycle-by-cycle laser ablation

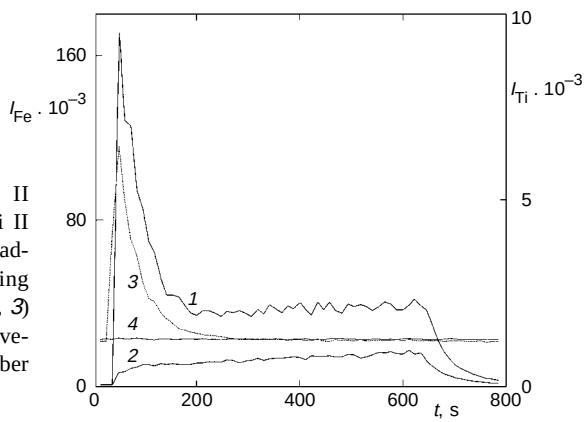

FIG. 1
Time-dependent behaviour of the Fe II 259.940 nm line intensity (*1, 2*), the Ti II 334.941 nm line intensity (*3*) and the adjacent Ti background intensity (*4*) during the continuous ablation of nitrided steel (*1, 3*) and untreated steel (*2, 4*). The laser wavelength 355 nm, energy 2 mJ, total number of cycles 41

was performed[2]. The results are given in Fig. 2 where the time-dependent behaviour of the Fe and V line intensities was given for the first three cycles. The energy was 2 mJ at 266 nm. As mentioned in Experimental, both Fe and V lines were measured simultaneously. From Fig. 2 can be seen that the maximum intensity of both Fe and V was obtained during the first cycle, i.e. in a layer of less than 0.6 μm (Table I). Both signals decreased during the second cycle. The V signal observed during the third cycle was resulting from the V content in the steel itself (1.85%). A high correlation was obtained between the Fe and V signals (Fig. 3), even when the transient signal exhibited a complex structure like that obtained during the second cycle. This structure could be partly explained by an heterogeneity resulting from an irregular diffusion between the layer containing V and the remaining part of the nitrided layer. However, the V/Fe line intensity ratio was different in the first and second cycles (Fig. 3). This high correlation implied that Fe and V (or Ti) were in the same chemical form in the nitride layer. In any case, the sputtered V (or Ti) was observed in a layer of about 1 μm, which is far

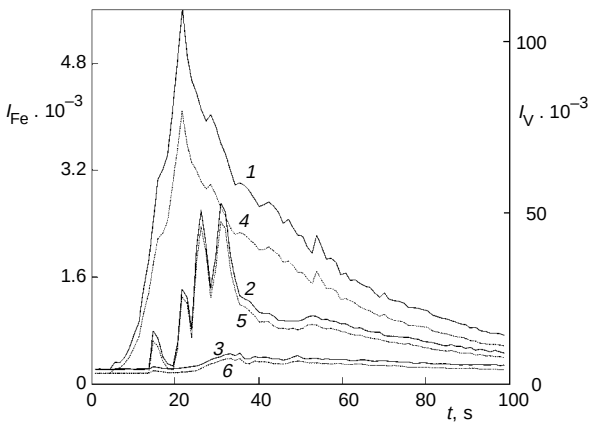

FIG. 2
Time-dependent behaviour of the Fe II 259.940 nm line intensity (*1*, *2*, *3*) and the V II 309.311 nm line intensity (*4*, *5*, *6*) for the first three ablation cycles performed on nitrided steel with sputtered vanadium. Laser wavelength 266 nm, energy 2 mJ. Curves: 1st cycle: *1*, *4*; 2nd cycle: *2*, *5*; 3rd cycle: *3*, *6*

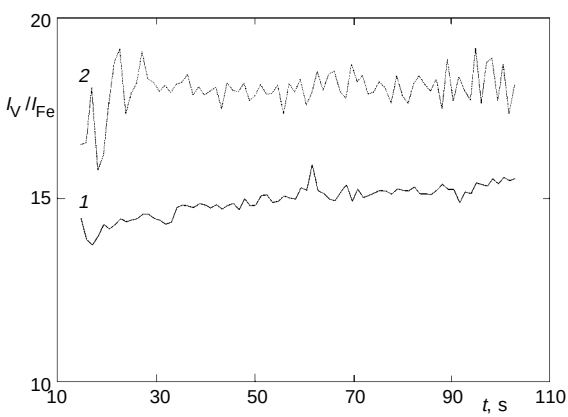

FIG. 3
V/Fe line intensity ratio as a function of time during the first cycle (*1*) and the second cycle (*2*) from the data shown in Fig. 2. Target: a nitrided steel with sputtered vanadium

less than expected (20 μm). Although it was not possible to provide quantitative results at this stage of the work, laser ablation had the potential to verify the spatial distribution of elements such as V or Ti in a layer of less than 1 μm.

Effect of the Operating Parameters on the Time-Dependent Behaviour of the Line Intensities

The influence of the laser wavelength on the time-dependent behaviour was found to be rather complex. The peak intensities of the transient signals observed during the first cycles are given in Fig. 4. The same energy, 1 mJ, was used for both wavelengths. The use of the 266 nm wavelength led to a drastic decrease in the Fe line intensity. The signal was decreased by a factor of 20 for the first cycle. In contrast, the use of the 266 nm wavelength led to an increase in the Ti line intensity. However, it should be noted that the line intensity of Ti was significantly lower than those of Fe and V, and the change was less drastic than for Fe as the increase was by a factor of 3 for the first cycle. Therefore, the trend observed for Ti was not necessarily significant. In any case, as mentioned above, the depth and the diameter of the craters after 3 cycles were similar irrespective of the wavelength, i.e. 0.8 and 250 μm, respectively. This means that the total production of the aerosol was similar whereas the particle size distribution was probably different.

For a given wavelength, relation between the line intensity and the crater depth was more logical. Figure 5 shows the Fe and Ti line intensities as a function of the laser energy at 355 nm. The corresponding crater depth obtained under the same conditions (Table I) is also given in Fig. 5. It can be seen that there was a good correlation between the Fe line intensity and the crater depth. This means that the energy modified the total amount of aerosol but probably not the particle size distribution, in contrast to what was observed for the influence of the wavelength. The results were rather erratic for Ti. This could be explained by the low Ti signal.

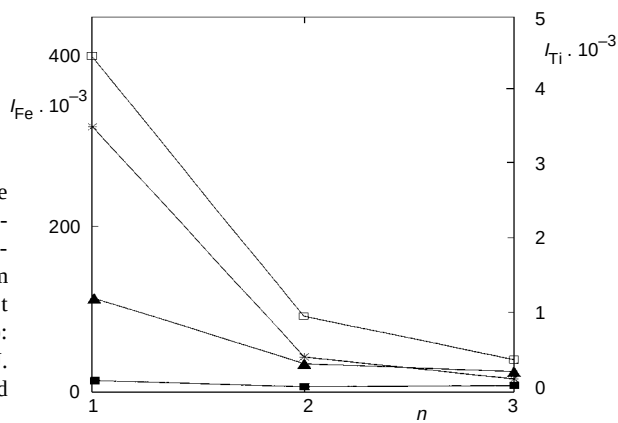

FIG. 4
Effect of the laser wavelength on the peak intensities of the transient signals of the Fe II 259.940 nm line intensity (❐, ■) and the Ti II 334.941 nm line intensity (*, ▲) during the first three cycles. Laser wavelengths (nm): 266 (■, *), 355 (❐, ▲); energy 1 mJ. Target: a nitrided steel with sputtered titanium

The influence of the laser energy and the nature of the target are shown on the peak intensity of the Fe and V transient signals for the first five cycles in Fig. 6. The two energies were 0.8 and 2 mJ at 266 nm. It can be seen that the use of the lowest energy, 0.8 mJ, led to a lower erosion rate. It was, therefore, necessary to perform five cycles to reach the untreated steel. For an energy of 2 mJ, only three cycles were necessary to reach the untreated steel. After five cycles, the depth was 1.0 and 1.3 μm for 0.8 and 2 mJ, respectively (Table I). This confirms that a better depth resolution was obtained at the lowest adjustable energy of the laser, i.e. 0.8 mJ at 266 nm. The curves in Fig. 6 confirm that a higher energy produced a higher signal, which is in good agreement with the erosion rate. The signal of Fe was enhanced by a factor of 3 for the first cycle while the signal of V was only slightly enhanced. This behaviour was similar to that observed for a change in the wavelength where the variation in the intensity was more important for Fe than for the sputtered element. Figure 6 indicates also the drastic decrease by a factor of 20 at 0.8 mJ of the Fe signal when untreated steel was ablated. As mentioned

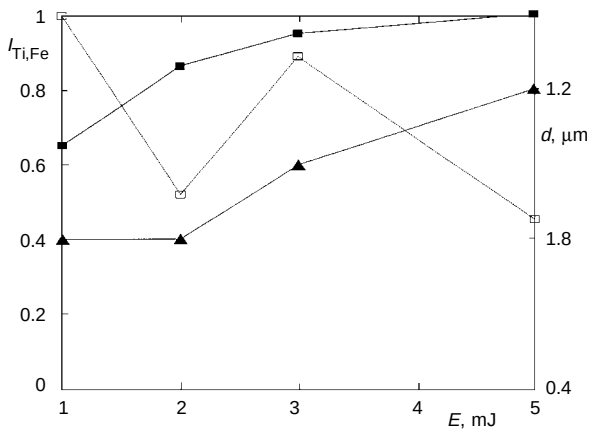

FIG. 5
Effect of the laser energy at 355 nm on the normalized Fe II 259.940 nm (■) and Ti II 334.941 nm (❒) peak intensities obtained after the first two cycles, and on the corresponding crater depth d (▲). Target: a nitrided steel with sputtered titanium

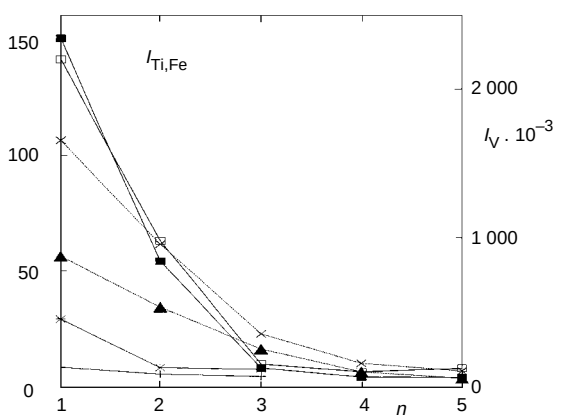

FIG. 6
Effect of the laser energy at 266 nm and the nature of the target on the peak intensity of the Fe II 259.940 nm line intensity (■, ▲, *) and of the V II 309.311 nm line intensity (❒, ×, +) during the first five cycles. Laser energies (in mJ): 0.8 (Δ, *, ×, +), 2 (■, ❒). Targets: untreated steel (*, +), nitrided steel with sputtered vanadium (■, ▲, ❒, ×). Scale expanded by a factor of 10 for untreated steel (*, +)

above (Fig. 1), it was obvious that the ablation efficiency was significantly different in the nitrided layer and the untreated steel.

CONCLUSIONS

Nitridation and sputtering of elements leading to nitrides with a high hardness influenced significantly the properties of surface of steel so that laser ablation efficiency was drastically modified compared with that observed for untreated steel. It was found that the sputtering of Ti and V during the nitriding processes led to the presence of these elements in an external layer of less than 2 μm. This evaluation was made possible by using a successive series of single laser ablation cycles resulting in an erosion rate of less than 0.5 μm per cycle. This was achieved by using an Nd:YAG laser with an energy per pulse in the UV which was limited to 1 mJ.

The effect of the laser energy and wavelength was rather complex as the results were different for the Fe line intensity and the sputtered element line intensities. The Fe line intensity was very sensitive to a change in these two laser parameters. In contrast, the change was different and less significant for the line intensities of the sputtered elements. The influence of the laser energy was logical in terms of signal intensity of the Fe line and crater depth whereas the role of the wavelength was not clear. Two laser wavelengths were used, 355 and 266 nm. For the same energy and number of cycles, similar shapes of craters were obtained whereas the signals were significantly modified. In particular, the Fe line intensity was drastically enhanced when the 355 nm wavelength was used in contrast to the sputtered element line intensities which were slightly decreased. A likely explanation is that the total amount of aerosol was similar for both wavelengths while the particle size distribution was changed differently for Fe containing species and Ti (or V) containing species, resulting in different transport efficiency, and evaporation and atomization rate in the ICP.

The optimum conditions for both depth resolution and signal intensity of the sputtered elements were achieved by using 0.8 mJ and 266 nm.

Although the influence of the laser energy and the laser wavelength was different on Fe and the sputtered element line intensities, a high correlation was observed for the Fe and Ti (or V) transition signals. This probably indicates that these species were present in the same chemical form in the nitrided layer and that the ablation processes were similar. Irrespective of the wavelength, the Fe signal was found to be the highest during the first cycle, although the concentration of Fe was not assumed to be the highest in this region. This means that the ablation efficiency was not constant even over a limited depth range of 5 μm. This was confirmed by the study of the erosion rate by means of profilemetry. At least for this type of sample, this is probably a severe limitation for the quantitative determination of sputtered species in the nitrided layer as the ablation efficiency varies with the depth. This contrasts with what was found for ZrN, TiN and ZrTiN coatings on steel[2]. At present, the depth of penetration of the sputtered elements

into the nitride layer can be determined within a few tenths of a micron based on the use of line intensity, but the absolute distribution of these species cannot be found because the results depend on both the content and the physical properties of the nitrided layer. More experiments will be carried out on steels with different nitriding depths. In any case, better knowledge of laser ablation could be obtained if adequate reference materials were available, in particular concerning the depth distribution of sputtered elements.

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