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The use of zinc and iron emission lines in the depth profile analysis of zinc-coated steel

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Abstract

In this study we report on the results of experiments devoted to the depth profile analysis of zinc-coated steel samples using the laser-induced breakdown spectroscopy (LIBS) technique. The dependence of zinc and iron emissions in three ablation atmospheres (air, argon, helium) was measured using the fundamental wavelength (1064 nm) of the Nd:YAG laser. The highest possible depth resolution was achieved by optimizing the experimental parameters, such as the delay time (which affects the tailing of the zinc emission signal), focusing conditions, energy delivered to the sample, and choice of buffer gases. Current research indicates that there is a constant need to optimize these parameters so that reliable depth-profiling analysis can be performed.

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1. Introduction

Nowadays several different techniques are employed for depth profiling of multilayered metal materials. Secondary ions mass spectrometry (SIMS) [1], X-ray photoelectron spectroscopy (XPS) [2], Auger electron spectroscopy (AES) [1,2], electron probe microanalysis (EPXMA) and total reflection X-ray fluorescence spectroscopy (TXRF) [3] are widely used (separately or combined with chemical etching or ion sputtering) for depth profiling on a nanometric and sub-micrometric scale. Glow discharge optical emission spectroscopy (GD-OES) [4,5] is very often applied to quantitative depth profiles of coated metal samples in the range from tens of nanometers to tens and hundreds of micrometers.

Pulsed laser ablation (LA) techniques are also powerful tools for depth profiling layered materials. In LA inductively coupled plasma atomic emission spectrometry (LA–ICP-AES) the ablated material is transported by carrier gas to an ICP and detected through atomic (optical) emission spectrometry. LA–ICP-AES has been used by Kanický et al. [6,7] to perform the depth profiling of a glass coated with a single layer of Sn, steel coated with partially stabilized zirconia, a graded metal–ceramic zone and NiCrAlY alloy layers. In LA inductively coupled plasma mass spectrometry (LA–ICP-MS) the ablated matter is carried in a gas stream to an ICP and detected by mass spectrometry. Coedo et al. [8] used a commercial highly focused (Gaussian) nanosecond UV (266 nm) Nd:YAG laser ablation system coupled to an inductively coupled plasma quadrupole mass spectrometer as a tool for the depth profile analysis of a copper coating on steel. Depth resolution, obtained from normalized in-depth profiles, increased linearly with the coating thickness. For the eight studied samples the ablation rate was approximately 1 μm/pulse. The feasibility of depth profiling of ZrTiN coatings was studied by Kanický et al. [9] using a 193-nm ArF* excimer laser ablation system with a lens array-based beam homogenizer in combination with an

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ICP-MS. The same system using LA–ICP-AES combined with a Nd:YAG laser (1064 nm) has been used to perform the depth profiling of zinc-coated iron sheets in the work of Hrdlička et al. [10]. The comparison of IR-LA and UV-LA profiles indicates that the material-dependent ablation characteristic of the metals is significantly different and the reliable metal ablation for depth profiling needs to change from a nanosecond to a femtosecond laser ablation system.

Laser-induced breakdown spectrometry (LIBS) is based on the detection of photons emitted by the atomized sample constituents in the laser-induced plasma created during laser ablation. In recent years LIBS has been applied successfully to the depth profiling analysis of metal samples with different coatings. Nanometric range depth-resolved analysis of coated steels was reported by Vadillo et al. [11]. The use of a flat energy profile XeCl excimer laser beam in LIBS has been demonstrated as an excellent way to generate craters with an improved depth resolution of up to 8 nm/pulse [12]. The capability of laser-induced breakdown spectrometry to resolve complex depth profiles has also been demonstrated by Vadillo and Laserna [13]. Electrolytically deposited brass samples were analyzed by monitoring the emissions corresponding to Cr, Ni, Cu and Zn emission lines. In the next work [14], a detailed description of the effect of laser irradiance on the averaged ablation rate and depth resolution of Ni–Cu-coated brass samples was presented. Analysis of layered materials using laser-induced plasma spectrometry was also compared with laser-ionization time-of-flight mass spectrometry [15]. St-Onge and Sabsabi [16] used a Nd:YAG laser 1064 nm for quantitative depth profiles of three elements (Al, Fe and Zn) on two galvannealed samples. For the calibration of the iron and zinc line intensities, the iron-to-zinc intensity ratio was used and it was assumed that the sum of the iron and zinc concentrations was equal to unity everywhere. The position of the coating substrate interface was estimated by a method based on finding the most negative value of the second derivative on the line intensity profile for the major element in the coating. A steel sample coated with titanium nitride has been depth profiled by laser-induced plasma spectroscopy in an ultraviolet vacuum by Radivojevic et al. [17].

The surrounding atmosphere has a significant influence on the laser-induced plasma characteristic. Time-resolved measurements of temperatures and electron densities of laser-produced plasmas generated in air, argon and helium at atmospheric pressure have been presented by Aguilera and Aragon [18]. The plasmas were obtained by focusing a Nd:YAG laser on a low-alloyed steel sample. Higher temperatures and electron densities were obtained in argon; a faster decrease of measured temperatures and densities takes place in helium. Spatial characterization of laser-induced plasmas obtained in air and argon with different laser focusing distances has also been reported [19].

The delay time, i.e. the time between laser pulse and detection of emission also plays a key role in the evaluation of the signal from the LIBS. The time selection significantly influences the signal/noise ratio. A short time after the laser pulse the signal is dominated by background radiation. However, the background emission decreases faster than the line emission of the sample constituents. A short delay time also plays a significant role in the self-absorption effect. In principle, the timing parameters (delay and integration times) are highly dependent on the element and the matrix, and must be optimized for each sample [20].

2. Experimental

In order to study the depth profile, zinc-coated iron sheets were ablated using a Nd:YAG laser system (Quantel, Brilliant). The laser operated at the fundamental wavelength (1064 nm) with a pulse width of 4.4 ns, beam diameter 5 mm and repetition rate 10 Hz. The energy of the laser pulse was monitored by an energy meter (Nova-Ophir, Optronics).

The laser-induced sparks were produced by focusing the laser beam with a 170 mm focal-length glass lens. Different power densities on the sample surface were achieved by defocusing the laser light.

Utilizing a gas-filled laboratory-made aluminum ablation chamber with a quartz window, the depth-profiling in different ablation atmospheres (air, argon and helium) was studied (at atmospheric pressure). The 18 cm^3 chamber was mounted so that the focused laser beam was inclined at 72° to the sample and the observation angle of the objective was at 90° to the sample surface.

The laser-induced plasma (LIP) radiation was collected with a quartz objective and transported by a 3-m fiber optic system onto the entrance slit of a 0.32 m monochromator (Jobin Yvon TRIAX 320). The monochromator was equipped with three interchangeable holographic gratings of 1200, 2400 and 3600 g/mm. In this study the grating of 2400 g/mm and entrance/exit slits of 50 μm were used. A photomultiplier (Hamamatsu C1392) gated by a laboratory-built control unit was employed as a detector. For the gate-time delay monitoring and time-resolved signal recording, a digital storage oscilloscope Tektronix TDS 1012 was used. The wavelength scale of the spectrometer was calibrated using an ICP source with a nebulizing solution containing 100 mg l^{-1} zinc or iron. A schematic drawing of the experimental setup is shown in Fig. 1.

The time-resolved emission signal (with a resolution of 10 ns) at the given wavelength was recorded for the each laser shot and the final temporal evolution of the LIP emission was obtained by averaging 16, 64 and 128 laser shots.

The depth profile was evaluated by measuring the intensity of the zinc atomic line at 280.08 nm (background intensity was measured at 279.30 nm) and the iron atomic line at 344.06 nm (background intensity was measured at 343.30 nm). The zinc, iron and background signals were obtained by firing the laser at laterally displaced sites on the sample for consecutive measurements.

For visual inspection and documentation of the created ablation craters a digital camera (Nikon Coolpix 5000) connected to a binocular microscope (PZO Warsaw, Poland) was used. The optical profilometer (Fries Research & Technology GmbH, MicroProf FRT) with a CHR 150 N sensor was utilized for crater depth measurements.