Microanalysis of tool steel and glass with laser-induced breakdown spectroscopy

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A laser microscope system for the microanalytical characterization of complex materials is described. The universal measuring principle of laser-induced breakdown spectroscopy (LIBS) in combination with echelle optics permits a fast simultaneous multielement analysis with a possible spatial resolution below 10 pm. The developed system features completely UV-transparent optics for the laser–microscope coupling and the emission beam path and enables parallel signal detection within the wavelength range of 200–800 nm with a spectral resolution of a few picometers. Investigations of glass defects and tool steels were performed. The characterization of a glass defect in a tumbler by a micro-LIBS line scan, with use of a 266-nm diode-pumped Nd:YAG laser for excitation, is possible by simple comparison of plasma spectra of the defect and the surrounding area. Variations in the main elemental composition as well as impurities by trace elements are detected at the same time. Through measurement of the calibration samples with the known concentration of the corresponding element, a correlation between the intensity of spectral lines and the element concentration was also achieved. The change of elemental composition at the transient stellite solder of tool steels has been determined by an area scan. The two-dimensional pictures show abrupt changes of the element distribution along the solder edge and allow fundamental researches of dynamic modifications e.g., diffusion in steel. © 2003 Optical Society of America

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1. Introduction

For the characterization of complex samples with macroscopic properties, determined significantly by the microscopic structure, microanalytical methods are required. The local analysis of the elemental composition of tiny sample areas is important for various technical applications, e.g. the investigation of textures, the characterization of thin layers and material defects and contaminations. Classical laboratory methods for element analysis, such as the flame and graphite furnace atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry do not enable microanalytical investigations. Moreover, they are very expensive and time consuming owing to the necessary sample preparation.

In past decades electron probe microanalysis in combination with energy–wavelength dispersive x-ray analysis have been established as methods for the analysis of the smallest amounts of material. The display of the elemental composition within the sample is possible with a high spatial resolution. The method requires a very time-consuming sample preparation; the measuring range has to be diluted and a good conductivity of the sample must be provided. In combination with the necessary sample insertion into a vacuum system, the measuring time can be up to several hours. Semiconductors and insulators can be measured either with problems only or not at all.

Laser induced breakdown spectroscopy (LIBS) is characterized by the spectral analysis of a laser-induced plasma.1–4 The analysis of the emitted lines allows the direct analysis of the atomic composition of substances. The “pure optical” measuring principle permits the analysis of main and trace elements within a few seconds. Since laser light can be focused well, the smallest amount of material can be analyzed with dimensions of few micrometers. The quasi-punctiform evaporation of material allows the simple and fast detection of local inhomogeneities along the sample surface as well as the detection of depth profiles.

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The first experiments with LIBS used for microanalysis by a coupling of the laser source with a microscope have been published in the recent years.\textsuperscript{5,6} Disadvantageous were the low spectral resolution, the small simultaneously detectable wavelength range, and the more or less experimental laboratory setup of the measuring system.

In this paper a laser microanalyzer is introduced, permitting a local-resolved simultaneous multielement analysis in the range of few micrometers. The new measuring system allows a significantly faster analysis, because no extensive sample preparation is required and the system is working under normal atmosphere.

The capabilities of the system will be discussed using selected applications, e.g. the analysis of glass defects and the local-resolved imaging of elemental distribution in tool steel. In particular for the local-resolved measurements in glass, no alternative methods are available. Especially, the electron spectroscopy as the method of choice often leads to a wrong interpretation of results, owing to the insulator properties of glass and the corresponding charge effects.\textsuperscript{7}

2. Experimental Setup

The schematic diagram of the microscopic laser-induced plasma analyzer is shown in Fig. 1. The instrument consists of five main components: a compact Nd:YAG laser, the laser beam positioning and focusing optics, the microscope, the echelle spectrometer unit, and the electronic part for control and spectra processing. The emitted laser pulses are transmitted over the beam expander optics and the illuminator unit into the optical path of the microscope. The microscope objective focuses the laser light onto the sample and collects the emitted plasma emission. Between the mirror and the objective the laser beam and the emitted plasma radiation have the same optical axis, resulting in the ability to perform depth profile measurements. By means of the ocular lens the measuring signal is directed to the entrance of a fiber taper and transmitted to the spectrometer entrance. To observe the sample, a tiltable mirror enables the use of a television camera. The optical analyzer unit consists of an echelle spectrometer with an intensified camera system. Here the spectral splitting and the image of the plasma emission on the sensor takes place. The intensified CCD sensor consists of a CCD array coupled with a gated microchannel plate image intensifier. The control system synchronizes the image intensifier, the detector, and the laser unit, as well as the \(x, y\)-motorized translation stage at the microscope table. The system also defines the delay and the integration time of the intensified camera system, temporally shifted to the plasma-generated laser pulse. An integrated personal computer is used for data analysis and measuring control.

The microscope system features a completely transparent UV optics system for the detection of the UV range down to 200 nm. The desired optical properties were achieved through the modification of the beam path inside a standard microscope (Axioskop, Zeiss, Germany). The system has a powerful infinitesimal color-corrected system optics systems with objectives with infinite image distance. Owing to the parallel beam path between the objective and the tubus lens, additional components may be added with use of a plug-and-play method, without optical components for compensation.

Tubus and collimator lenses were then replaced by quartz lenses. With the reflector slide of the microscope, dielectric mirrors can be slid in, guiding the laser radiation to the objective. Particular frequency filters have been developed, resisting the laser radiation and featuring a high-reflection degree for the corresponding excitation wavelength, as well as a high transmission for the entire relevant wavelength range of 200–800 nm.

Mirror objectives (15\(\times\)/0.28, Ealing Electro-Optics, Holliston, Massachusetts) and quartz lens objectives (10\(\times\)/0.20 and 40\(\times\)/0.50, Ultrafluar, Zeiss, Germany) were tested. At high laser power only the mirror objectives were used, featuring higher working distances.

The working range of the \(x, y\)-translation unit is 75 \(\times\) 25 mm\(^2\), with a repetition accuracy of <1 \(\mu\)m. Its control unit is video based, permitting a punctual control.

The coupling optics between the laser and the microscope can be adapted to the laser excitation wavelength. The optics realizes a beam transformation and interimgaging to adapt the beam cross section to the free lens diameter of the microscope and thereby reduces the acting power density on the optics. A Q-switched Nd:YAG-pulse laser (Minilite, Continuum, Santa Clara, California; beam diameter 3 mm,
pulse width 6 ns, repetition rate 10 Hz) has been used for excitation. The maximum pulse energy was 50 mJ at 1064 nm and 4 mJ at 266 nm (fourth harmonic generation). Additionally, a diode-pumped Nd:YAG-laser (DIVA, Thales Laser, Orsay, France; beam diameter 2 mm, pulse width 10 ns, repetition rate 20 Hz) with TEM$_{00}$-beam profile was tested for the determination of the maximal achievable spatial resolution. The maximal pulse energy was 20 mJ at 1064 nm and 5 mJ at 266 nm.

The use of an echelle spectrometer (LLA Instruments, Berlin, Germany) in combination with an intensified CCD-sensor array (KAF 1001, Kodak, Rochester, N.Y.) permits the time-resolved measurement of fast plasma processes with high spectral resolution (5–18 pm) at simultaneous detection of a wavelength range of 200–800 nm. The spectrometer system, optimized for laser plasma analysis, was developed in cooperation with Institute of Spectrochemistry and Applied Spectroscopy. The applied optical principle is shown in Fig. 2. An echelle grating, positioned under a flat angle of incidence, produces up to 100 diffraction orders. An additional quartz prism in front of the grating separates the overlapping orders by splitting them vertically to the direction of the spectrum. In that way the compact spectrograph covers a total spectrum length of over 1 m on a one-square-inch (1 in. = 2.54 cm) focal plane. The simultaneous recording of the complete relevant spectral range from 200 to 800 nm with a linear dispersion of approximately 5 to 18 pm/pixel is possible. Owing to the positioning of a large pixel sensor array into the focal plane of the spectrograph the simultaneous detection of nearly all analytical lines of interest with a high spectral resolution is achieved and enables a real multielement analysis. The control software permits a free programmable binning (on-chip addition) for the selective readout of defined pixel areas on the CCD matrix. A spectrum image on the sensor array may be binned; that way that only areas relevant for the analytical evaluation are used, and unnecessary spectral ranges are discarded. Thus the readout of the CCD array is controllable, depending on the analytical task and the elements to be detected.

The complete analysis with use of just one laser shot is a precondition for local resolved measurements. The measuring program permits the parallel detection of all elements within one measuring step.

3. Results and Discussion

The primary goal of the following investigations was to demonstrate the possibilities of a laser microscope system for microanalytical characterization of complex materials. The results are given and discussed on the examples of stellite-tool steel and glasses. Previously, qualified measuring and the operational parameters for the local plasma analysis subject to material ablation, thermal stress of the sample, and achievable spatial resolution were determined. Influences of laser parameters, e.g. excitation wavelength, laser pulse energy, and laser beam profile, were analyzed.

A. Optimization of Spatial Resolution and Detection Sensitivity

The measurements with a flash-lamp-pumped Nd:YAG pulse laser at an excitation wavelength of 1064 nm showed high thermic stress at the generated holes. Metal samples showed melting areas on the borders of the created holes. Metal, glass; 266-nm excitation: (a) metal, (b) glass; 266-nm excitation: (c) metal, (d) glass.

The achieved craters feature a smaller diameter and significantly “cleaner” edges [Figs. 3(c)–3(d)]. Pulse energies of 4 mJ were high enough to produce a stable plasma excitation for both material
the detection limit decreases significantly. At a high spatial resolution with crater diameters below 10 μm, approximately \(10^{14}\) atoms occur in the plasma. For 10 ppm an absolute detection limit of \(10^9\) atoms is necessary. Therefore, subject to the analytical task, a compromise between the required spatial resolution and the element-specific detection limit always must be found.

Therefore the advantage of a diode pumped laser, featuring a better laser beam quality enabling a higher spatial resolution, often could not be used. When the diode current is controlled a simple controlling of the laser energy is possible at constant beam quality. Hence, the change of the pump power of a flash-lamp-pumped laser influences the beam divergence, since the thermic lens inside the YAG-stick, i.e. the pulse stability and beam quality, is affected.

Optimization of the temporal gating (delay to laser pulse, exposure time) improves the signal-to-noise ratio. Adaptation of the timing of the image intensifier yields a useful suppression of the fast-decaying continuum radiation with high intensity in order to separate it from the atomic emission, used for analysis. The measurements show very short decay times, less than 1 μs. Typically, delay times of few 100 ns have been applied, and a nearly noise-free background was obtained. In particular working at 266 nm excitation the gate must be selected carefully; a small temporal shift results in a strong loss of line intensity or in a fast line broadening and an increase of background signal.

B. Investigation of Tool Steel Samples

First microanalytical investigations on tool steel were performed. The strong stress on the tempered cutting edges of tool steel during treatment demands suitable physical properties of the material, e.g. abrasiveness, and temperature-, wear-, and edge stability. The local analysis of the chemical composition of the smallest areas of the material gives necessary the information for reasons for reduced abrasion resistance. For the characterization of material inhomogeneities an exact quantitative analysis is not necessarily required. It is sufficient to characterize the nature of the defect by a simple estimation of the modification of elemental composition between basic material and defect. The analysis of intensity of element-specific spectral lines permits a simple qualitative analysis. If an element is selectable as an internal standard, i.e. its concentration is almost constant, the use of intensity ratios is preferred. The quasi-punctiform excitation allows a defined investigation of microscopic small changes.

Figure 5 displays parts of the measuring protocol for multielement analysis for a carbide metal. The measurement was done with 350-ns delay to laser pulse, and an exposure time of 5 μs per laser shot. The spectrum parts used for analysis are shown (approximately 400 pm per line). In the example the simultaneous detection of nine spectral lines within a wavelength range of 280–515 nm was applied.
Above the detected line the peak area is given as quantum for intensity, as well as the line-intensity ratio to the Fe line.

The analysis of the carbid metal showed W, Ti, and Co as main components, characterizing abrasion and temperature resistance. Ta, Si, and traces of Cu, Fe, and Cr were found with low concentration. This evaluation is based on a comparison of spectral line intensities of known standard carbid metal alloys. Tungsten carbide with addition of the viscosity-increasing bond metal cobalt and a mixture of titanium carbide for a better oxidation resistance are particularly suitable for steel machining.

The basic material for the tool is a steel alloy with Mn and Si and a small amount of Cu and Cr. Because of the easier access to classified steel samples and the potential to use the common internal standardization method (for example see Ref. 10), a quantitative analysis is simpler in this case but was not subject to an investigation.

Microscope pictures of the cutting edge of the steel sample, a tool with soldered carbid metal, are shown in Fig. 6. The transition area basic material-solder-carbid metal is shown before and after the plasma analysis by a line scan. By use of the measured spectra an immediate qualitative analysis of the elemental composition was obtained. The measured line intensities along the performed line scan show the change of the composition for the transition area (Fig. 7). The spatial resolved measurements vertical to the solder edge indicated the diffusion processes of several elements, e.g. Si and Fe into the Cu solder. An area scan permits entire element distribution pictures. Figure 8 shows the absolute line intensities for the elements Fe, Cu, and Ti, depending on the position in the material. The sample was screened point by point with an area pattern of 90 μm. A comparison of the obtained two-dimensional profile for the element distribution with the corresponding microscope picture (Fig. 6) proved to be in good accordance with the relief of the sample. An abrupt change of element composition along the sol-
der edge was detected. Additionally, an enhancement of Fe inside the Cu solder was found along the entire joint.

C. Semi-Quantitative Analysis of Glass Defects
The method described in this paper was applied for the analysis of glass. Owing to the high transparency of this material, the human eye can easily detect each inhomogeneity, resulting in high-quality standards during glass production. If point defects or striae occur during the production process, the immediate determination of the reason for the defect is required.

Normally, a semi-quantitative analysis is sufficient for the characterization of the defect, performed by the comparison of the plasma spectra obtained from the defect and the surrounding material. The processing of spectra was performed as described above for tool steel. Figure 9 shows different defects in a tumbler: a gas bubble and a local inclusion.

To determine the reason for the defect we performed a microanalysis along the arrow. The diode-pumped Nd:YAG laser at 266 nm was used for material evaporation and excitation. Owing to the steady ablation of material by a high stability of the laser pulse, no additional correction of the measured line intensities was required. The absolute intensities of a Si, Ca, and Al line independent of the position are given in Fig. 10. In comparison with the surrounding glass matrix, the line scan showed a strong increase of Al content inside the defect, whereas the Ca content decreased; the concentration of Si varied slightly. Such defects are typical for corrosion with an Al₂O₃-containing ore, featuring a high melting point. The reason for the defect could be attributed to the aggregate.

For a detailed quantitative analysis a calibration of the measuring system using a set of standard samples is required. Glasses of known composition were provided by Schott Glaswerke (Mainz, Germany) and Zentrum für Glas- und Umweltanalytik (Ilmenau, Germany). A variety of standards with strong differing oxide content were measured to determine strong variations of concentration and to obtain a calibration for different glass sorts. Through measurement of these calibration samples a correlation between intensity of the spectral line and the element concentration was achieved for the samples.

A typical calibration curve is given in Fig. 11 on the example for determination of the relative CaO content. The line intensity ratio as a function of the concentration ratio to SiO₂ is shown. Silicon as the main component of the glass matrix was used as reference element. The curve features a satisfactory linear correlation. Changes of concentration between the matrix and the point defect can be estimated on the basis of the calibration curves.

Fig. 8. Elemental distribution along the solder edge of a tool steel (area scan).

Fig. 9. Microscope pictures of glass defects in a tumbler. (a) bubble, (b) inclusion (knot).

Fig. 10. Modification of the element composition (line scan) across the knot cross section.

Fig. 11. Calibration curve for quantitative glass analysis.

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Regarding SiO₂ content the Al₂O₃-content inside the defect varies between 5.5% and 25% in contrast to a relative content of 0.71% in the matrix. The relative content of CaO decreases from 12.2% to 4.25% in the center of the defect.

For the calculation of the absolute content, the complete detection of all elements is required. This is necessary because the concentration of the reference element (Si; specifically, SiO₂) may vary depending on the concentration of the minor components. If calibration curves exist for all oxides, a quantitative analysis of any glasses is possible through simple “shooting” on the sample and processing of spectral line intensities. The software of the introduced system supports the calibration procedure by calibration routines and algorithms for quantitative evaluation. Glasses with strong deviations to each other, referring to elemental composition, might require a particular calibration for each sort. Therefore an improvement of the result by a reduction of systematic errors is achievable.

Considering that even in homogeneous glasses considerable pulse-to-pulse variations of the spectral line intensities were observed, the quantitative estimation with standard deviations up to 10% are sufficient for the intended purpose. Changes in the material–laser interaction lead to remarkable fluctuations of the plasma excitation temperature and density. To improve the quantitative determination of the main components, different steps were taken. The microscope allows the precise adherence of the measuring distance at the various sampling points. The use of the fourth-harmonic generation of the diode-pumped Nd:YAG laser permits a more regular plasma excitation because of the significantly higher absorption coefficient of glass materials in the UV range. If possible, ratios of intensities were taken from lines, which have the same ionization stage and similar energies of the transition levels. In this case the ratios become more independent of variations in the plasma temperature. For example, for the signed calibration curve of the relative CaO content (Fig. 11), the following spectral lines are detected: Ca(I) λ = 442.544 nm (higher state, 4.68 eV; lower state, 1.88 eV) and Si(I) λ = 390.553 nm (higher state, 5.08 eV; lower state, 1.91 eV). With the used echelle spectrometer the available spectral window under observation is so large that the probability of proper lines for better compensation of changes in the material–laser interaction is significantly higher than with classic spectrometers.

4. Conclusions

The laser plasma analyzer developed for microanalytical routine measurements features a fast simultaneous analysis of any chemical element with a spatial resolution down to 5 μm. The measuring technique does not require an extensive sample preparation and can be performed without protective gas.

Variations of the main composition and contamination by trace elements can be detected simultaneously. The element-specific detection limits are in the range of 10–100 ppm.

By means of selected applications, i.e. the analysis of glass defects and the detection of two-dimensional pictures of elemental composition of tool steels, the capabilities of the system could be demonstrated successfully. The results indicate the possibility of an at-line analysis of glass defects. A simple semi-quantitative microanalysis of defects in glass indicates the source for the defect. Impurities in the basic material can be identified and characterized. Additionally, the monitoring for element contamination within the parts-per-million range is possible. An alternative and particularly fast method for the microanalytical characterization of glass composition is now available.

The results for tool steel prove the possibility of an analysis for quality control during production process (analysis of defects and contamination). Basic research of the influence of dynamic changes in tool steel, owing to corrosion, diffusion, or mechanical or thermic stress is also possible. The measured local element distributions are in good agreement with the morphologic changes of the sample in the microscope picture.

The technique described in this paper is applicable to many other applications. New application fields for the laser microanalyzer are foreseen in the scientific area. Investigations of textures and grain boundaries, the evaluation of layer structure, and the characterization of dynamic changes are possible.

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References


