SPECTRAL ANALYSIS OF THIN SOLID FILMS[1]

A. BRABLEC[2], V. KAPIČKA[2], Brno

The usual thickness attained in polymer films prepared by high frequency sputtering of metal in a carrier gas is 0.5 μm. In the present paper a method is suggested how to evidence the presence of basic elements in these films also by the LMA 1 laser microanalyser and by the spark discharge.

СПЕКТРАЛЬНЫЙ АНАЛИЗ ТОНКИХ ТВЕРДОТЕЛЬНЫХ ПЛЕНОК

Обычная толщина полимерных пленок, получаемая при помощи высокочастот-
ного распыления металла несущим ратом, равна 0,5 мкм. В работе предложен
метод доказательства наличия основных элементов в указанных пленках при
помощи лазерного микроанализатора и искрового разряда.

I. INTRODUCTION

The LMA 1 laser microanalyser by Carl Zeiss Jena is used to determine the chemical composition of a material in the required place of the investigated sample. The principle of this method is relatively simple. The laser pulse is focused on the place chosen before, where the local evaporation of the material occurs. Then this material ionises the space between two carbon electrodes, on which the voltage is set lying just below the value of the breakdown one. The arisen spark is analysed by a spectrograph in a standard way (the spectrum is recorded on a photographic plate). In conjunction with the QU 24 quartz spectrograph the LMA 1 equipment allows to evidence the existence of all ususal elements with atomic number 3—92, except gases contained in air, some lanthanoids (Pm, Eu, Tu, Lu), and with the exception of the Pa actinoid, some elements such as P, S, Po, Fr, Ra, Ac; if we use carbon electrodes carbon cannot be proved either. The analysed material need not be formed in a special way and in spite of some imperfections in the methodics of applying the LMA 1 the mentioned equipment may be used for a relatively rapid

identification analysis at small skill. The LMA 1 is first of all assigned to the microstructural analysis of steel, but as a matter of fact it is a universal equipment [1].

II. METHOD, EXPERIMENTAL CONDITIONS

The element may reliably be given evidence in the spectrum provided its evaporated mass does not exceed 10^{-11} kg, which depends on the burning of the crater with a diameter of 50 μm and a depth of 25 μm approximately. This is the question of route-identification values only, since the needful quantity of material is different for a reliable analysis with individual elements. It also depends on setting the working parameters of the laser microanalyser. However, it is evident from the experiments that the films with a smaller thickness than 10 μm cannot be analysed. The successful increase of polymer films prepared by highfrequency sputtering of the metal can be evaluated by the presence or absence of metal in the sputtered film. Besides, it is necessary to know the chemical composition of thin films. The typical thickness of those films moves about 0.5 μm, i.s. approximately 100-times smaller than the usual standard analysis by means of LMA 1.

The above requirement of a minimum material quantity (10^{-11} kg) cannot be avoided. We can obtain this quantity in the following way:

a) using a multiple exposition of the spectrum from different places of the film. However, there must be obtained disproportionately many expositions here (~100). The producer advises a maximum of 5 expositions with regard to the overlapping of measured lines by the CN, C_2 spectra, etc. Besides, the film is so thin in this case that we nearly analyse the substrate. For this reason the method is inapplicable.

b) by enlarging the diameter of the crater. This possibility, however, goes to the detriment of the microanalysis, i.e. the investigation of the chemical composition in a area of the surface as small as possible. But, in our case, this fact is of less importance, since we are interested in the global composition of the film only.

The diameter of the crater (and/or the area that is employed for analysis) may either be enlarged by blooming the laser or so that the carbon electrodes are approached closely to the surface of investigated film and a spark jumps between the electrodes, evaporates the film on the substrate between them and thus, the required material may come into the spark. Both methods were investigated in detail.

The following films were subjected to the analysis:
1) An Ag film of about 100 nm thickness (deposited onto the glass substrate);
2) a Zn film of about 100 nm thickness (deposited onto the glass substrate);
3) a Zn film of about 500 nm thickness (sputtered onto the glass substrate at a pressure of about 10^3 Pa in a nitrogen atmosphere film is loosened) and

4) an unknown polymer film of about 500 nm thickness (deposited onto ethe glass substrate).

To find the possibility of analysing such film thicknesses, the films 1, 2 were taken as the testing ones. Silver evaporates well and its two characteristic lines are sufficiently intensive (328.0683 nm, 338.2891 nm). Zinc has three characteristic lines (328.2333 nm, 330.2588 nm, 334.5020 nm), which are 2.5-times thinner than the Ag lines, approximately. Zinc evaporates worse, it has a higher melting point than Ag. The mentioned metals were chosen as the testing ones for their simple line spectra and easy preparation of the film with a required thickness (evaporation). Zinc was also chosen to make the identification of the Zn lines in film No. 3 more precise, for the QU 24 spectrograph has a mean dispersion only.

III. EXPERIMENTAL CONDITION

The distance of the carbon electrodes was always the same, 0.001 m, the distance of electrodes from the films was about 0.001 m (when the laser was used), cca 0.002 m (in case of spark discharge), resp. The spark parameters: $L = 60$ μH, $C = 2$ μF and/or $C = 1$ μF. The discharge lamp voltage was always at a maximum, i.e. 2 kV. Then the output energy is about 1 J. If the diameter of the laser beam (on the surface of the sample) is 10—20 μm, the power density is 10^{11}—10^{12} W/m² (the mean time of the pulse is about 10^{-4} s) [1]. In our case the laser worked in a so-called uncontrolled regime. ORWO WU 2 plates were used, processed in a standard way. The spectral line strength was both assessed visually and measured by a G 2 photometer.

IV. RESULTS

There were recorded about 15 spectra of the investigated samples (1, 2). The obtained information can be summed up as follows:

1. *The occurrence and determination of lines and molecular band in the spectra.*

a Besides the Zn spectral lines, which are of interest to us, there are still other lines observed in the spectra: CN, C_2 molecular spectra, a carbon line spectrum. Lines of elements such as Re, Ti were also found in the spectrum, whose occurrence in our case is improbable. It seems that those elements are from air (some lines of oxygen, nitrogen) — or from the carbon electrodes, since they appear in all the spectra. The contamination may also be due to the manipulation with the sample. This is valid for Ca mainly, whose lines (422.6728 nm, 399.8468 nm, 393.3666 nm) are observed irregularly in all spectra. If we determined the spectrum of the carbon electrodes only then, the Ca lines might fairly be differentiated from those of the investigated sample.

2. *Determination of the influence of the blooming of the laser beam.*

Ag 328,0683
328,2330
Zn 330,2590
330,2940
334,5020
Zn 334,5570
334,5930
Ag 338,2890

CN 359,0400

386,1900
387,1400
Ca 388,5400
C 392,0680
CN 393,3666
396,8458

In 407,6000
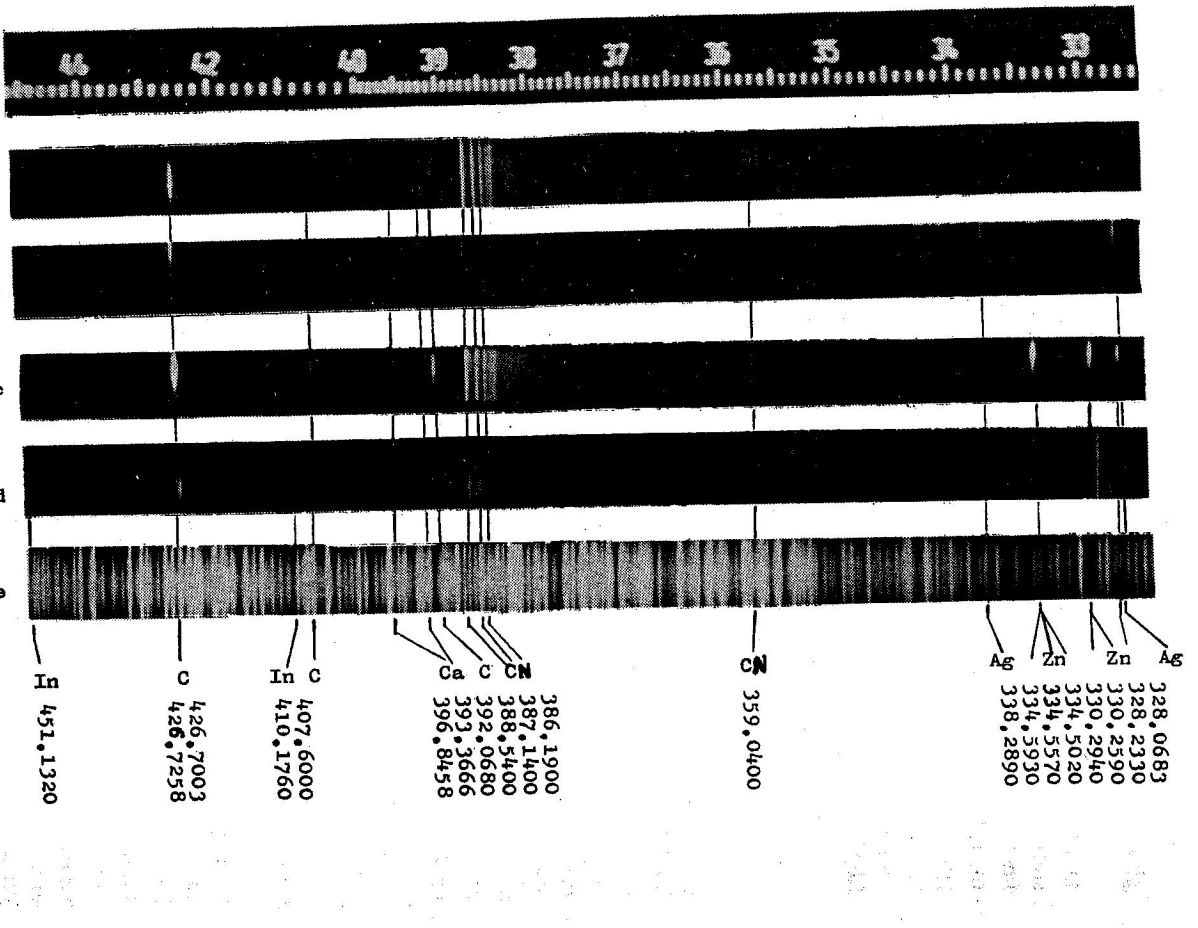C 410,1760

In 426,7003
C 426,7258

In 451,1320

Fig. 1. Spectra obtained in the analysis of thin films by the LMA 1 equipment: a) the spectrum of the carbon electrodes, b) sample No. 1 — Ag film, c) sample No. 3 — Zn film, d) sample No. 4 — polymer film, e) Fe spectrum.

In this case we bear in mind the blooming of the observed picture by the microscope. The picture is focused somewhat below and/or above the film (the micrometer screw allows the transport of the lens by 1 μm). Thus the film will be struck by the laser beam with a larger diameter. It was observed that the influence of the laser pulse has here the dominant role, but the spark which jumps between the electrodes. As to the difference between the laser focusing below and above the film it was observed that the Ag line appears stronger when we focuse upon the film below. However, it is necessary to remark that the samples 1, 2 have a mirror surface and, therefore, it was not easy to focus the picture onto the surface of the sample precisely. The influence of the blooming of the laser beam on the diameter of the crater and its depth is shown in Fig. 2 (for two elements Zn, Cu). It was also observed that using the laser the spectrum was less rich in lines.
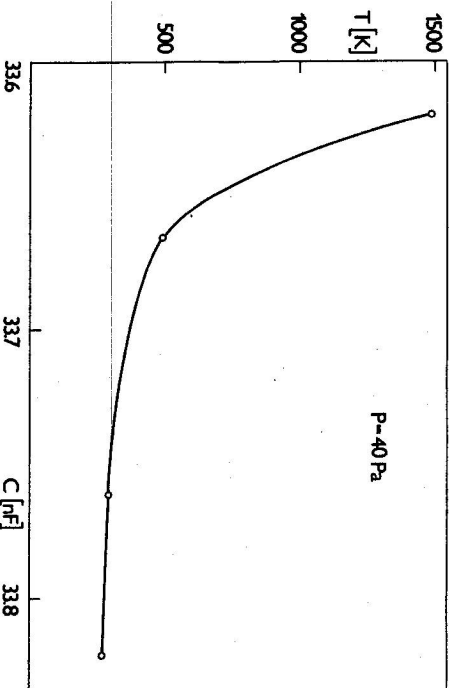

Fig. 2. The size d and the depth h of the crater as a function of the blooming of the laser beam (+ ... the transport of the lens towards the film surface — ... vice versa).

3. The use of the spark in the analysis of thin films.

The spark, which jumps between the carbon electrodes, is strong enough to make a sufficient quantity of material to evaporate for the proper analysis. This evaporation takes place, more or less, on the surface without complicating the film spectrum analysis by the substrate elements. It depends, naturally, on the quantity of the film material, which is being evaporated. For example, on the area of the Ag film about 5×10^{-3} m in diameter, the evaporated quantity was much less than in case of Zn, which has been enough for a reliable analysis. The influence of the spark on the sample surface was followed in the Ag film. If the distance of the

electrodes was 1×10^{-3} m, then the Ag lines were not found until at a six times larger distance of electrodes from the sample surface. The temperature of excitation (from the Zn lines in case of the spark discharge) and the vibrational temperature (from the CN molecular lines) were determined. In the first case we obtain the mean value 8300 K, in the second 6200 K. Similar measurements were made in [3] but for the case of the laser. The results are the same in order as ours under the comparable conditions. The discharge both with and without laser was recorded by a high speed camera. From the equidensities, which were made from these figures (see also [3]), we can conclude on the size and shape of the discharge. It is also possible to determine the distance of the film from this discharge.

A certain problem is the sticking of the film material to the carbon electrodes, making the lines from the previous analysis to appear consequently in the spectrum of the new film. Cleaning by the spark helps with metals with a higher melting point, when not so much material is evaporated as in the case of Ag. Here it is necessary to use new carbon electrodes for every analysis, and/or to clean the electrodes in some suitable way. So far we use new electrodes, the results are reproducible.

V. DISCUSSION AND CONCLUSION

This method has made it possible to analyse the sample 3, 4.

The Zn line intensity was so strong that the existence of Zn may be proved at even smaller thicknesses. It is reasonable to analyse films with thicknesses of about 100 nm. It depends on the investigated element and on its quantity in the film as well. In sample No. 4 In was proved to be the main element of the given polymer film, which corresponds to the composition of the primary material.

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