Abstract
The effect of laser treatment on copper irradiated by a Nd:YAG laser was investigated by optical microscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Wettability measurements were taken previously on the laser treated samples and the results showed interesting changes. In this paper the surfaces of the copper samples were analyzed with optical microscopy, SEM, XPS and AES in four laser power parameter. The SEM observations demonstrate that in this laser beam power range the level of surface modification is not affected by the laser power. According to the XPS and AES results we can say that the measurements do not show exact connections between the oxidation state and the wettability of the laser treated surface.

Keywords
laser treatment, copper, XPS, AES, wetting

1 Introduction
For high technology manufacturing the use of lasers in materials processing is an attractive choice. Because of this we need better understanding of the physical and chemical aspects of materials processing (Markovits and Bauernhuber, 2014; Wang et al., 2002). It is claimed that laser surface treatment has the greatest growth potential in the field of laser materials processing. Application of laser technology in metal surface modification takes advantage of heat energy from the laser beam to alter the materials’ surface properties. Laser processing has more advantages over the conventional methods which include local heating of the surface without changing the substrate material properties, precision and high speed of operation, and low cost (Kalyon and Yilbas, 2003). Laser surface treatments offer a wide range of possibilities to achieve desired surface properties. The principle of laser surface treatment is the modification of a surface as a result of interaction between a beam of coherent light, with high power density, and the surface within a specified atmosphere (vacuum, protective or processing gases). The formation of a modified layer is determined by the laser processing parameters settings. Some laser parameters are laser beam wavelength, continuous-wave (CW) or pulsed mode, temporal pulse power (pulse length, peak power and pulse shape), repetition rate, beam energy distribution, and beam geometry including focal spot size and depth of focus (Olsen and Alting, 1995). Control of parameter settings also yields different effects on the modified surface properties. Though several types of laser have been used in laser surface processing, the laser power and scan speed or material laser interaction time were observed to have a strong influence on the resulted temperature profile, modified layer depth, and mechanical, corrosion and tribological properties of the processed surface (Mioković et al., 2007; Mondal et al., 2008). Circular laser spot profiles produced by the TEM\textsubscript{00} mode are generally suitable for most laser applications. Furthermore, the melt pool formed by the TEM\textsubscript{00} depth and width, and develops more quickly during processing compared to other modes (Han and Liou, 2004). During the past years, a number of researches have clarified the effects of the laser irradiation on different material surfaces, such as metals,
semiconductors, polymers and multilayer materials. There are a lot of important aspects of the laser material interactions which are responsible for the change in structure, composition and chemical state of the irradiated surface of the material. In recent studies it has been shown that laser irradiation may modify the surface composition and structure of metals and alloys, which increases their resistance to wear and corrosion (Pereira et al., 2002; Zeng et al., 1995). For example, the laser irradiation of iron and other metals in a nitrogen atmosphere or in air leads to surface nitration that is known to improve the hardness and corrosion resistance of the materials (Copola et al., 2002; Schaal, 2002; Stefanov et al., 2006). It has also been found that laser treatment of a steel surface in air promotes the incorporation of oxygen and nitrogen into the surface, thus leading to formation of different crystalline phases (ferrous oxide or nitride) (Pereira et al., 2002; Pereira et al., 2004; Stefanov et al., 2006). However, very little work has been focused on improving the material’s wettability by modifying surface properties of materials by laser (Zhao et al., 2006).

The use of copper in electronics increases, as it is needed for personal computers, cellular phones and telecoms expansion (Stefanov et al., 2006). Laser processing of copper has its inherent problems due to its high reflectance and its very high thermal conductivity (Zeng et al., 1995, Panagopoulos and Michaelides, 1992).

In our previous work we experimentally determined the wetting property changes in the copper following the Nd:YAG laser treatment. The changes in surface energy were investigated by the contact angle measurement of solders on copper (Hlinka et al., 2017). The wetting experiments were performed in a wetting angle measuring system (Hlinka and Weltsch, 2013) which can measure the wettability using sessile drop method (Abtew and Sobczak, 2000), taking the methodological issues summarized by Sobczak (Sobczak et al., 2005) into account. The measurements were performed in air atmosphere at 523 K temperature.

Results are shown in Fig.1. The wetting properties are mostly influenced by the surface layer that is the reason why the surface analysis is important after the laser treatment.

The grain boundary segregation has a paramount importance in the laser-treated surfaces (Kaptay, 2016).

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy (KE) and number of electrons that escape from the top 1 to 10 nm of the material being analyzed (Wagner, 2011).

Surface specificity arises from the limited flight path an electron has within a solid before it loses some fraction of its energy (this is generally less than 10 nm). The X-rays can penetrate micrometers below the surface but if energy is lost, the signal will disappear within the spectral (Heide, 2012). The spectrum obtained is a plot of the number of emitted electrons per energy interval versus their kinetic energy. The kinetic energy of the photoelectron (KE) is the difference between the X-ray photon energy $\hbar \nu$ ($\hbar$ is the Plank’s constant and $\nu$ is the X-ray frequency) and the binding energy (BE) of the core-level electron (Wagner, 2011). The binding energy may be regarded as the energy difference between the initial and final states after the photoelectron has left the atom (Moulder and Chastain, 1995).

Each element has a unique elemental spectrum, and the spectral peaks from a mixture are approximately the sum of the elemental peaks from the individual constituent. Since the mean free path of the electrons is very small, the electrons which are detected originate from only the top few atomic layers. Quantitative data can be obtained from the peak heights or areas and identification of chemical states often can be made from the exact positions and separations of the peaks, as well as from certain spectral contours (Wagner et al., 1979).

X-ray photoelectron spectroscopy (XPS) allows establishment of the chemical composition of the surface and the chemical state of the components. Auger electron spectroscopy (AES) is suitable for mapping the lateral distribution of the elements.

In this paper we examined the laser treated copper samples with optical microscopy, SEM, XPS and AES to get some information about the surface.

2 Materials and methods

In order to analyze the influence of the laser treatment on microstructure, the specimens, before and after laser treatment, were sectioned with a cutting machine using a diamond-rimmed cutting blade. The sectioned specimens were mounted with epoxy then, subsequently, polished with a cloth and diamond suspension paste down to 1 µm. The cross sectioned samples on the copper surface were examined, respectively, by optical microscope and SEM. SEM investigations were carried out using a SEM equipment Philips XL-30 FEG SEM machine.
2.1 Laser treated copper

The wetting angle of solder pastes were examined on Cu ETP R240 (CW004A) copper plates as substrates. This type of copper is widely used for electrical and electronic applications. Before the measurements the copper plates were grinded and polished to remove the oxide layer and reach similar surface properties in every sample and washed with 96% ethanol (C\textsubscript{2}H\textsubscript{6}O) (Hlinka et al., 2017).

The laser used in the study was Rofin DY 027, Nd:YAG pulsed laser with emission of 1064 nm wavelength laser beam. The laser beam was focused directly onto a 0.4 mm diameter spot on the surface of copper plate. During the laser surface treating process, the laser beam was traversed across the copper samples by means of a laser scanner at speed of 500 mm/min. The laser scanning speed must be controlled properly to ensure that a 40 x 40 mm square area can be treated by laser. Different laser powers were used in this process. The laser was used in continuous wave and TEM\textsubscript{00} mode. Argon gas was used as shielding gas to protect the samples from oxidation during laser irradiation with the flow-rate of 12.5 l/min (Hlinka et al., 2017). The laser machine and the layout of the treated samples were shown in Fig. 2.

Fig. 2 Rofin DY 027 Nd:YAG laser and the layout of samples

The measurements in this paper were carried out on the untreated copper sample and on the laser treated samples which are treated by 300 W, 600 W and 2500 W laser power.

2.2 XPS and AES measuring instrument

The chemical composition and the chemical states of the elements at the surface were measured by XPS (Fig. 3). In order to characterize the lateral inhomogeneities, electron-excitation Auger electron spectra were recorded at points on surface.

The XPS and AES analyses were carried out in the same analytical chamber at a base pressure of 5 × 10\textsuperscript{-9} mbar. For XPS, we used Mg K\textalpha\textsubscript{a} (1253.6 eV) radiation (without monochromatization) from a twin-anode x-ray source (VG Microtech XR3E2). For AES analyses, the electron beam of a VG Microtech LEG200 source at 3 keV and 1 μA was used. The photo- and Auger electron spectra were taken with a truncated hemispherical analyzer (VG Microtech Clam2).

Fig. 3 Complex equipment makes in situ or quasi-in situ XPS and AES measurements possible during simulated technological process steps (controlled exposure to heat, gases, plasma, ion irradiation) (dept.phy.bme.hu)

3 Results and discussions

3.1 Surface microstructure after laser irradiation

Fig. 4 shows the surface layer microstructures of the optical metallographic samples before and after laser irradiation with different laser power.

As may be seen by comparing Fig. 4 a)-d) the laser treatment did not cause noticeable changes on the copper surface layer. The observations indicate that when the laser power was 2500 W, the heat absorbed by copper could not lead to the formation of molten pool which is typical in case of laser surface treatments. The absorptivity of different metals depends on the wavelength of the radiation. The used Nd:YAG laser has a wavelength of 1064 nm. The absorptivity of copper at this wavelength is 2–3% (Beyer and Wissenbach, 1998). The surface roughness measurements of the laser treated surfaces shows similar results. The roughness parameters effect on the wettability, that is why important, that the laser treatment did not change the roughness parameters of the surfaces.

Fig. 4 Optical microphotographs of the surface layer microstructures after laser irradiation with different laser power: a) untreated, b) 300 W, c) 600 W, d) 2500 W (Hlinka et al., 2017)
3.2 SEM observations of treated surfaces

A Scanning Electron Microscope was used for analysis of the laser treated surfaces. Fig. 5 shows the top surfaces of untreated and laser treated (300 W, 600 W and 2500 W) samples. The surface of Cu substrates are almost flat, however after laser treated random ridges and grooves were produced. Using laser irradiation a fraction of the laser beam energy is absorbed by the material, thus promoting material melting, surface morphological modifications and the formation of a thermal oxide layer. The comparison among the SEM pictures reported in Fig. 5 demonstrates the effect of the laser process parameters. The SEM observations demonstrate that in this laser beam power range the level of surface modification is not affected by the laser power.

![Fig. 5 SEM image of the Cu surface after laser irradiation with different laser power: a) untreated, b) 300 W, c) 600 W, d) 2500 W (Hlinka et al., 2017)](image)

3.3 XPS measurements

First we recorded on the laser treated Cu samples the Cu2p and X-ray induced Cu LMM Auger spectra. The binding energies of the Cu2p, Cu LMM lines give information about the oxidation state of the copper samples which treated with different laser powers. Then we recorded the C1s and O1s core level spectra and after that we recorded one more time the Cu2p, Cu LMM spectra. Finally with lower resolution and higher sensitivity we recorded a “complex review” spectra to see whether there are any other components on the surface.

We recorded the spectra this order because as experience shows that in case of sensitive samples the heat generated by the X-ray gun and the X-ray radiation cause changes on the sample surface.

In general, we can give two types of information about the sample surface. We can calculate the percentage of the surface compounds from the peaks of intensity and we can define the bonding conditions. For most elements (e.g. carbon) the more the peak shifts toward the higher binding energy, the atom is belonging to a more oxidized state. The copper behaves differently. For copper the extent of this so-called chemical shift quite small. Instead of this on the Cu2+ spectra the Cu2p3/2 and Cu2p1/2 peaks become wider, and two satellite peaks can be appearing in. In less oxidized copper atoms these effects are much weaker. In case of Cu+ state barely visible in practice.

The LMM Auger peaks of copper are more sensitive to the bonding state changes. The peak position of pure Cu metal is at 918.6 eV kinetic energy which shifts to 917.7 eV in case of Cu+ and shifts 916.8 eV in case of Cu2+ and become more unclear.

Based on the first copper spectra of the samples surface it seems that all four surfaces contain Cu2+. The samples which treated by 300 W and 2500 W seems to be more oxidized from the four samples (Fig. 6). These are fairly look like spectra from the surface of a compound which is containing Cu2+ ions. The form of satellite peaks is not quite like we expect in case of pure CuO. Based on this it could be something hydroxide (XPS can not see hydrogen), or perhaps something carbonates on the surface.

![Fig. 6 Core level Cu 2p spectra of the untreated and the 300 W, 600 W 2500 W laser treated copper samples](image)

In case of the untreated sample and the sample which treated by 600 W laser power the satellite peaks intensity lower and the peaks of Cu2p3/2 and Cu2p1/2 look different. On the right side of the peak grows a sharper peak which suggests that they are a lower oxidation state of copper atoms on the surface. Based on the Cu LMM Auger peaks this is likely to be metallic copper (Fig. 7). Probably the surface ‘coating’ layer of these samples are thinner and beneath the copper is in the XPS information depth and it also appears in the spectra. Based on the first recorded Cu2p peaks we can say that in case of the sample which treated by 600 W laser power there is the least amount of oxidized Cu atom.
The repeated Cu2p, Cu LMM spectra look like as they recorded from a surface which contains Cu+ ions. In other words, whatever was on the surface, it degraded relatively short period of time. The heat produced by the X-rays and the X-ray gun is probably decomposed the compound and thus retained in the surface of the less oxidized state.

In case of oxygen two different bonding state can be separable (Table 1). The A component which is probably in a metal oxide, and B component which is in a metal carbonate or in organic impurities deposited on the surface.

**Fig. 7** Auger LMM spectra of the untreated and the 300 W, 600 W 2500 W laser treated copper samples

**Table 1** Bonding states of measured oxygen on the samples surfaces

|       | A (%) | B (%) |
|-------|-------|-------|
| 0 W   | 29.8  | 70.2  |
| 300 W | 20.4  | 79.6  |
| 600 W | 32.4  | 67.6  |
| 2500 W| 20.3  | 79.7  |

**4 Conclusion**

In summary based on the XPS measurements we can say that the surfaces of the 300 W and 2500 W laser treated copper samples were more oxidized, but this oxidized layer decomposed during the XPS measurement. The wettability measurements of the laser treated copper samples and the XPS and the AES surface analyzing measurements do not show similar results. The changes measured by the wettability measurements can not be explained by the XPS and AES results. The optical microscopy and SEM observations demonstrate that the laser did not cause noticeable changes on the copper surface layer and microstructure in this laser beam power range.

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