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Analysis of copper surface features obtained using TEA CO_2 laser at reduced air pressure

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ABSTRACT

Interaction of a transversely excited atmospheric (TEA) CO_2 laser with rough copper surface, at reduced air pressure, was studied. Optical pulse duration of the laser employed was ~2 μs, with the initial spike FWHM of ~100 ns. Laser energy density of ~32 J/cm^2 (intensity ~10^8 W/cm^2) was above the plasma ignition threshold. Morphological features of the copper can be summarized as follows: (i) superficial damages, which take crater-shaped form at a higher number of accumulated laser pulses, (ii) development of melt pools with visible bubbles inside the damage region, (iii) formation of solid droplets at near periphery, and (iv) presence of "halo" effect at the irradiated surface. The laser induced surface changes were influenced by the target plasma formation. The formation of plasma influenced the laser–target interaction in two opposite ways: trough absorption of laser energy by the plasma, i.e. trough the effect of plasma shielding, and trough energy transfer from the plasma to the sample. Optical emission spectra were compared for laser induced plasma originated by a single and by cumulative laser pulses. It was found that plasma dimensions and emission intensities have a strong correlation with the number of accumulated laser pulses. Enhancement of both atomic and ionic copper lines was registered when laser induced plasma originated from a single pulse. Chemical analysis of the surface showed a tendency of copper content increase and oxygen content reduction when going from non-irradiated region to the central irradiated region. In the central damage zone, nearly pure copper was present which can be advantageous for some applications due to considerably lower contamination.

1. Introduction

Copper and copper-based alloys are in a category of highly important materials characterized by extraordinary properties. Copper exhibits desirable physical, chemical and mechanical properties [1], such as high electrical and thermal conductivity, excellent workability (ductility, brazing, soldering, welding), good corrosion resistance, good mechanical properties. Due to these characteristics, copper and its alloys are successfully applied in electronic industry (e.g. microelectronics), optics, aerospace engineering, and mechanical industry [2–4].

Modification of copper surface using lasers is intensively studied, particularly in the last two decades. Different types of laser systems including excimer [5,6], Nd:YAG [5,7,8], Ti:Sapphire [9,10], cw or pulsed TEA CO_2 laser [11,12] have been employed for these purposes. Typical laser intensities in these studies were in the interval from 10^9 to 10^{14} W/cm^2, while lower intensities (~10^8 W/cm^2), which are a subject of this consideration, were rarely employed. It is important to point out that consideration of the state of the matter, including solids, irradiated with laser intensities of the order of 10^8 W/cm^2 is essential for applications such as surface desorption and spectroscopy (plasma emission LIBS method).

Treatment of bulk copper target with a TEA CO_2 laser beam pulsed in the nanosecond time domain, with the intensity of the order of 10^8 W/cm^2, is still insufficiently studied in literature. Generally, many metals, including copper, have high reflectivity at wavelengths in the mid-IR spectral range [13]. In order to increase the absorptivity in this spectral region, different methods are applied. Thus, copper surface absorptivity was enhanced by coating with CuO/Cu_2O layer [11], plating with tin layer [12], or by surface chemical treatment (water solution with inorganic compound) [14]. Enhancement of the copper absorptivity by changing its surface roughness, applied in this work, is scarcely studied in literature. Namely, the reflectivity of polished copper mirror-like surface, which is very high at CO_2 laser emission wavelengths (>95%), can be drastically reduced if the rough surface is employed.

Our primarily goal was to study the effects of nanosecond laser (intensity ~10^8 W/cm^2) emitting in the mid-infrared (10.6 μm) on a rough copper bulk surface at reduced air pressure. Special attention was paid to morphological alterations of the surface.

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Chemical changes, particularly changes in surface oxide content were observed too. These variations, taking into account that irradiation was carried out at near vacuum conditions, can give information about the surface cleaning effect. At the applied laser intensities plasma appearance in front of the copper target was recorded and its spectral emission was studied as well.

2. Experimental

2.1. Sample preparation and characterization

The disk-shaped copper samples had a typical size of 35 mm diameter and 5 mm thickness. The sample surface with increased roughness was prepared by a metallographic procedure. The targets were mechanically treated with 320-grit SiC abrasive paper, ultrasonically cleaned, dried in hot air and kept in the desiccator. Such procedure created clearly visible, random, from 1 to 6 μm wide scratches on freshly-prepared copper surface (Fig. 1A). Beside scratches, other "imperfections" like micro-cavities and flakes were also visible. Just before irradiation the targets were carefully cleaned with ethanol.

The surface metrology of a rough copper surface was measured by a profilometer (Talynova). In addition, the Surface Metrology Algorithm Testing System, developed at the National Institute of Standards and Technology, was used to calculate the surface roughness [15]. The root mean square deviation of the assessed profile was 5.4 μm, while the maximum profile peak height and maximum profile valley depth were 7.9 and 4.0 μm, respectively.

In order to compare the specular reflectivity of polished and rough Cu targets, the polished samples were carefully prepared. These samples were firstly processed with 1200-grit SiC paper and then polished with 1 μm diamond paste. For the purpose of sample reflectance measurements, copper target was placed at the angle of ~20° to the direction of the incident TEA CO_2 laser beam. A sensitive pyroelectric detector was used for measuring specular reflectivity. Measured reflectivity values, of polished and rough copper surfaces, were 0.96 and 0.65, respectively. The measured reflectivity of rough copper surface was in good agreement with the data given in Ref. [16]. We presumed that, because surface roughness was smaller than the wavelength of the laser light, diffuse scattering was small compared to dominant specularly reflected light [17].

The ratio of the absorbed laser power to the incident laser power depends on several parameters including laser wavelength, angle of incidence, polarization, metal oxide layer thickness and structure, surface contamination, and surface roughness [17,18]. It is well known that surface roughness has a profound influence on metal target reflectivity, i.e. its absorptivity ($A = 1 - R$) [19]. It was also shown that the increase in absorptivity with roughness is most pronounced for metals that are very reflective in the flat, smooth state like Cu [17]. Impurities, on and in the metal surface, can also increase the absorption of radiation. One type of impurities are abrasive particles left behind by polishing, whose contribution to the absorption is largely determined by the species of embedded particles and their absorptivity properties at the laser wavelength [13]. Apart from impurities, additional absorption may be a consequence of bulk defects, such as pores, cracks, grooves and flakes. The role played by the different defects appears to be especially important in the irradiation of metallic targets with microsecond pulses generated by CO_2 laser sources, when in order to get the metal bulk vaporization, incident laser intensities of the order of 10^8–10^9 W/cm^2 are necessary [20]. The absorptivity of metal surfaces can also be changed due to the presence of oxide layers. The oxide layers can cause an increase in sample absorptivity by as much as an order of magnitude [21]. The thickness and the structure of the oxide layer are the main properties that determine this absorptivity contribution. The effect is mainly due to the interference phenomena occurring inside the layer where the beam is partly absorbed, partly reflected at the metal and partly reflected back again at the oxide-atmosphere boundary. Besides, it was found that the microstructure and the thickness of the oxide layers depend on the Cu surface roughness, i.e. thickness of the oxide layer increases while the average grain size of the oxide layer decreases with increasing the surface roughness [22,23]. Generally, the total absorptivity cannot be described only by the bulk properties of the metals but must also, and often to a large extent, include contributions from the surface conditions. The appreciable scatter in absorption data in the literature, and the often, large disagreement between data and the theory, mainly stems from the fact that the quality of the surfaces of the irradiated samples was not clearly specified. The most comprehensive and complete description of the subject may be found in a book "Laser Heating of Metals" by Prokhorov et al. [13].

In our case, several effects contributed (probably to a different extent) to changes of copper surface-air boundary: increased surface roughness, presence of native oxide layer (confirmed by EDX analysis) and possible contamination from surface polishing. The net effect of all of these contributions was the observed decrease of copper reflectivity.

Table 1
Typical parameters of the TEA CO_2 laser used during irradiation of a copper target.

Gas mixture content	$CO_2/N_2/He = 1/1/4.7$
Gas mixture pressure (atm)	1
Output pulse energy (mJ)	Up to 200
Energy density-fluence (J/cm^2)	Up to 35
FWHM[a] (ns)	~100 (initial spike)
Peak power (MW)	~0.70
Peak power density (MW/cm^2)	Up to 100
Mode structure	Multimode output (typical)
Spectral emission[b] (μm)	10.5709 and 10.5909
Repetition rate (Hz)[c]	Up to 2

[a] Full width at a half maximum. TEA CO_2 laser pulse consists of initial spike and a tail. The tail duration is about 2 μs. Approximately 35% of the total irradiated laser energy is consisted in the initial spike.
[b] TEA CO_2 laser simultaneously operates at two wavelengths, i.e. 10.5709 and 10.5909 μm, P(18) and P(20) transitions.
[c] Typical laser repetition rate used in this work was 1 Hz.

2.2. The laser source

The laser employed is a commercial TEA CO_2 laser system developed at the VINCA Institute [24]. It is a miniature, compact system. Its main characteristics relevant for the experiment are given in Table 1. Optical pulse had a gain switched peak followed by a slowly decaying tail. Full width at a half maximum of the peak was about 100 ns, while the tail duration was ~2 μs. About 35% of the total irradiated laser energy was consisted in the initial spike.

The laser beam was focused by a ZnSe lens of 135 mm focal length, and during the process of irradiation target surface was in the focus. The TEA CO_2 laser was run in a multimode regime. Samples were irradiated in a chamber evacuated down to the air pressure of 0.1 mbar.

2.3. Morphology and spectroscopy measurements

Various analytical techniques were used for characterization of the copper target surface before and after laser irradiation. Surface morphology was monitored by optical (OM) and scanning electron microscope (SEM). The signals produced by SEM include secondary electrons (SE), back-scattered electrons (BSE) and X-rays. Secondary electron images (SEI) were used for examination of the surface morphology. The intensity of the BSE signal is in a strong correlation with the atomic number of the specimen and