Applied Surface Science 302 (2014) 79–82

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Generation of nanoparticles of bronze and brass by laser ablation in liquid

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ARTICLE INFO

Article history:
Received 26 June 2013
Received in revised form 6 November 2013
Accepted 4 December 2013
Available online 12 December 2013

PACS:
42.62.−b
61.46.+w
78.66.−w

Keywords:
Nanoparticles
Laser
Ablation
Liquid
Brass
Bronze

ABSTRACT

Nanoparticles of brass and bronze are generated by ablation of corresponding bulk targets in liquid ethanol. The experiments were performed using three pulsed lasers with different pulse duration: ytterbium fiber laser (80 ns), a Neodymium:YAG laser (10 ps), and femtosecond Ti:sapphire laser (200 fs). The generated nanoparticles (NPs) are characterized by UV–vis absorption spectroscopy, X-ray diffractometry, Raman scattering, and Transmission Electron Microscopy. The size of generated NPs lies in the range 10–25 nm depending on the laser source. The X-ray diffractometry reveals the change of phase composition of brass NPs compared to the initial target in case of ablation with 80 ns laser source, while with 10 ps laser pulses this effect is less pronounced. Brass NPs generated with pico- and femtosecond laser radiation show the plasmon resonance in the vicinity of 560 nm and no plasmon peak for NPs generated with longer laser pulses. Raman analysis shows the presence of Cu_2O in generated NPs. The stability of generated NPs of both brass and bronze to oxidation is compared to that of Cu NPs generated in similar experimental conditions.

1. Introduction

Generation of nanoparticles (NPs) under laser ablation of solids either in gas or in vacuum has been extensively explored during last decade. Understanding of the mechanisms of clusters formation is needed to control the process of pulsed laser deposition (PLD) that is widely used now for deposition of a large variety of compounds. Formation of nanoparticles (NPs) under laser ablation of solids in liquid environment has been studied in much lower extent. Generation of both Au and Ni NP under ablation of corresponding solids by pulsed Nd:YAG laser has been reported in [1–3]. Later, the formation of NPs of Ag and other metals has been reported under laser exposure of metallic targets to laser radiation [4,5]. Alloyed NPs may be generated in two ways, either via laser exposure of colloidal solution in liquids or via laser exposure of a bulk target of an alloy. Synthesis of Ag–Au alloy in under laser exposure of suspension of core–shell Au–Ag NPs has been observed recently [6]. Both Ag shell removal from Au NP and their alloying has been observed depending on laser wavelength and its fluence. Alloyed NPs may also be generated by laser exposure of a mixture of colloidal solutions of individual NPs [7]. Copper is chemically active and easily reacts with vapors of surrounding liquid. The chemical interaction may take place both during the ablation and after it due to contact with air oxygen dissolved in the colloidal solution. Typically, the plasmon resonance of Cu nanoparticles lies in the visible. Cu NPs synthesized by chemical means in anaerobic conditions show the absorption peaks from 570 to 590 nm [11]. Laser ablation of Cu target in various liquids also leads to formation of NPs that are characterized by absorption in the visible [3]. The peak position is around 590 nm, which agrees with previously reported theoretical data for Cu NPs [8].

Laser ablation of Cu-containing materials leads to somewhat different NPs. For instance, ablation of a brass target (60% Cu, 40% Zn) in ethanol leads to formation of brass core–shell NP [9,10]. Similarly, ablation of a bronze target (92% Cu, 8% Sn) leads to formation of core–shell NP. It is worth mentioning that both brass and bronze NPs generated by laser ablation in liquid are characterized by their own plasmon resonances that do not coincide with that of pure components, Sn, Zn or Cu NPs. Brass NPs under further laser exposure of colloidal solution undergo internal segregation, namely,

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0169-4332/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.12.018

low melting point component (Zn) is pushed out to the periphery of NPs. The resulting absorption spectrum after laser exposure to nanosecond pulses transforms into plasmon resonance of pure Cu. This behavior is attributed to the difference in melting point of the components of brass NPs. Indeed, upon solidification of a brass nanoparticle Cu solidifies first, while Zn component remains liquid yet. This favors separation of the components in NPs. The dynamics of this separation should strongly depend on the duration of laser pulse through the rate of cooling. One might expect that under short or ultra-short duration of laser pulse the deviation of the stoichiometry of generated NPs from that of the bulk target will be less pronounced. Three different laser sources are used in present work to generate and characterize NPs of both brass and bronze in order to combine high conductivity of Cu-based materials with improved stability against oxidation by air oxygen. From the practical point of view this gives a hope that such NPs will be more stable against oxidation by air oxygen and, therefore, be of interest in ink jet printing of conducting electrodes for solar cells. This kind of ink uses polyvinilenepyrrolidon (PVP) as a surface-active substance, so in some cases PVP was added to the working liquid.

2. Experimental

Brass (27% Zn + 73% Cu) and bronze (13% Sn + 87% Cu) targets were used for generation of NPs. Laser ablation of a bulk Cu target was also carried out for comparison of optical properties of generated NPs. Laser ablation of targets was conducted in liquid ethanol. Surface-active substance PVP (polyvilenepyrrolidone) was added to ethanol in several experiments. Three different laser sources were used for generation of NPs. The first was a Ti:sapphire laser at wavelength of 800 nm and pulse duration of 200 fs at repetition rate of 1 kHz. The second was Yb-doped fiber laser with pulse duration of 80 ns at wavelength of 1062–1064 nm and pulse repetition rate of 20 kHz. The third laser was a Nd:YAG laser at wavelength of 1064 nm and pulse duration of 10 ps and pulse repetition rate of 50 kHz. Single beam of nanosecond laser was focused by the objective-glass with focal length of 22 cm. Diameter of the beam in focus was equal to 35 μm. In case of femtosecond and picosecond, focal length of the lens was 2 cm with beam diameter of 10 μm. The exposure time in experiments with nano- and pico-seconds was 30 min. Laser exposure of targets was carried out either in a flowing cell reactor (picosecond and nanosecond laser pulses) or in a cell rotating under the laser beam (femtosecond pulses). Due to high repetition rate of ps and ns lasers the linear velocity of the liquid flow under the laser beam was set to 1–2 cm s^{-1} for guaranteed detachments of gas bubbles from the exposed area.

The size distribution function of generated NPs was determined using disk measuring centrifuge CPS DC 2400. The morphology of generated NPs of brass and bronze was characterized with the help of a Transmission Electron Microscope Jeol. Raman spectra of dried NPs were acquired with the help of a Raman spectrometer Nicolette. X-ray diffraction data of dried NPs were collected with the help of an X-ray diffractometer operating at Cu Kα line.

3. Results and discussions

Size distribution functions of both brass and bronze NPs generated with different laser sources are presented in Fig. 1.

One can see that addition of PVP to the working liquid does not alter significantly the size distribution function. In general, longer laser pulses (80 ns) produce smaller bronze NPs with their size near 10 nm and narrow size distribution.

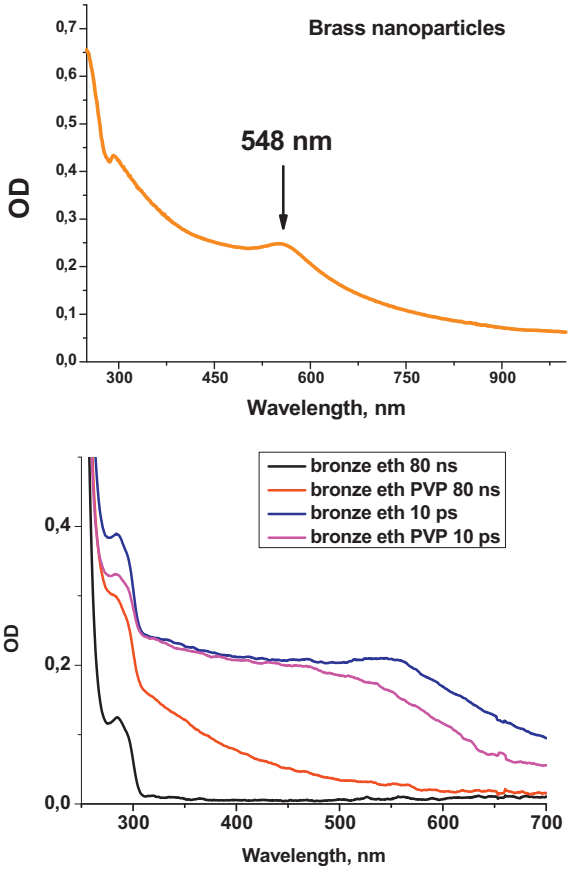

Fig. 2. Optical density (OD) of brass (a and c). Ablation with 200 fs laser pulses (a) and with 80 ns and 10 ps laser pulses (b and c).

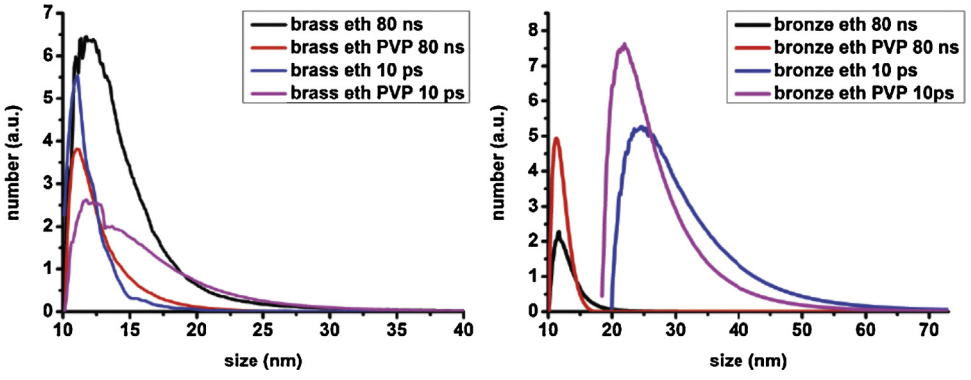

Fig. 1. Size distribution of both brass and bronze NPs generated at various durations of laser pulses.