Applied Surface Science xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

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

Influence of the reactive atmosphere on the formation of nanoparticles in the plasma plume induced by nanosecond pulsed laser irradiation of metallic targets at atmospheric pressure and high repetition rate

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ARTICLE INFO

Article history:
Received 21 June 2015
Received in revised form 9 October 2015
Accepted 15 October 2015
Available online xxx

Keywords:
Laser ablation
SAXS
Metal oxides stability
Nanoparticles

ABSTRACT

The influence of a reactive atmosphere on the formation of nanoparticles (NPs) in the plasma plume generated by nanosecond pulsed laser irradiation of metal targets (Ti, Al, Ag) was probed in situ using Small Angle X-ray Scattering (SAXS). Air and different O_2–N_2 gas mixtures were used as reactive gas within atmospheric pressure. SAXS results showed the formation of NPs in the plasma-plume with a mean radius varying in the 2–5 nm range. A decrease of the NPs size with increasing the O_2 percentage in the O_2–N_2 gas mixture was also showed. Ex situ observations by transmission electron microscopy and structural characterizations by X-ray diffraction and Raman spectroscopy were also performed for powders collected in experiments done using air as ambient gas. The stability of the different metal oxides is discussed as being a key parameter influencing the formation of NPs in the plasma-plume.

1. Introduction

Laser treatments are powerful tools for many technological processes such as welding, cleaning and marking. The formation of nanoparticles (NPs) is usually observed in metal targets irradiated by pulsed laser sources with a pulse duration less than a few tens of nanoseconds [1–5]. The ablation mechanism which is the origin of the NPs formation strongly depends on the laser pulse duration.

In nanosecond laser ablation, the expansion of the plasma-plume formed above the target can be quenched by the ambient gas at a high enough pressure giving rise to the formation of NPs. The composition and the pressure of the ambient gas strongly influence the properties of the NPs thus formed [4,3].

In this range, the absorption of the laser beam in both the target surface and the plasma-plume formed above the target surface by surface vaporization strongly depends on the laser wavelength. On one hand, the absorption depth of light in metals is more shallow in the visible than in the IR range. On the other hand, the absorption of the laser beam by the plasma-plume due to inverse Bremsstrahlung varying as λ^2 [6,7] and the absorption is higher in the IR range than in the visible. Hence, the ablative effect can be high in the visible range, whereas IR lasers induce a deeper and efficient heating of the target. The high energy of species in the plasma-plume favors the formation of NPs in the latter case. The laser plume undergoes a rapid spatial expansion, which is slowed down due to its compression in the surrounding atmosphere. Typical models of nanosecond laser ablation consist of several stages including the laser heating and evaporation of the target, the laser heating and expansion of the plasma plume and the condensation process giving rise to the formation of NPs [8–10].

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http://dx.doi.org/10.1016/j.apsusc.2015.10.090
0169-4332/

In femtosecond laser ablation, the laser pulse duration is shorter than the characteristic relaxation times and thus the laser-plume interactions are minimal or negligible [11,5,12].

In any case, for both nanosecond and femtosecond laser treatments, the ambient gas plays a key role in the process giving rise to the NPs formation. In situ probing the plasma plume is of great interest to understand the mechanisms of NPs formation.

Third generation synchrotron radiation based Small Angle X-ray Scattering (SAXS), allows in situ probing for the presence of nano and mesoparticles to be done in complex media. In previous works, we have used SAXS to study particle size distributions in diffusion flames [13], microwave-generated fireballs [14], electrical arcs [15] and also in the plasma plume induced by nanosecond IR pulsed laser irradiation of titanium targets in air [16]. In the latter case, we showed the existence of at least two families of nanoparticles formed in the plasma plume. The smallest, with radii of gyrations of about 10 nm, grow in the plume by condensation and then aggregate to form structures in the form of a necklace of about 55–75 nm in size, depending upon the irradiance of the laser [16].

In this paper, we report new results obtained using SAXS on the SWING beam-line at the SOLEIL synchrotron. The aim was to study the influence of a reactive atmosphere on the formation of NPs in the plasma plume. For this, laser treatments and in situ SAXS experiments were performed in an air-tight chamber which allowed the composition of the surrounding atmosphere to be controlled. In this way, various O_2–N_2 gas mixtures as well as common air were used. Moreover, the effect on different metal targets (Ti, Al, Ag) was also studied. For experiments in air the NPs thus formed were collected and studied ex situ using transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy.

2. Experimental details

In this experiment, the size and the morphology of the nanoparticles were studied for different compositions of both the irradiated metal target (Ti, Al, Ag) and the surrounding atmosphere. Pure Ar, O_2–N_2 gas mixtures with different percentages of O_2 and N_2, and common air were used. The oxygen volume content in the gas mixture was varied from 0% to 20%. A custom chamber (Fig. 1) was fabricated for this purpose. The target was placed on a motorized plate which provided a continuous displacement of the sample during the SAXS experiments in order to avoid any effects due to a modification of the target surface during the laser treatments.

The laser beam direction was kept fixed and perpendicular to the target surface. An optical window in BK7 transparent glass was used to reduce the absorption of the laser beam. Targets were irradiated with the fundamental harmonic of a Nd:YAG laser operating at 1064 nm, with a pulse duration of 5 ns and a repetition rate of 20 kHz. The laser beam irradiance focused on the target was 1.2 GW cm^{-2}. In previous experiments with a similar laser source irradiating a titanium target in air, the general shape of the plume was found to be hemispherical, its height and width being about 2.8 and 5 mm, respectively [17].

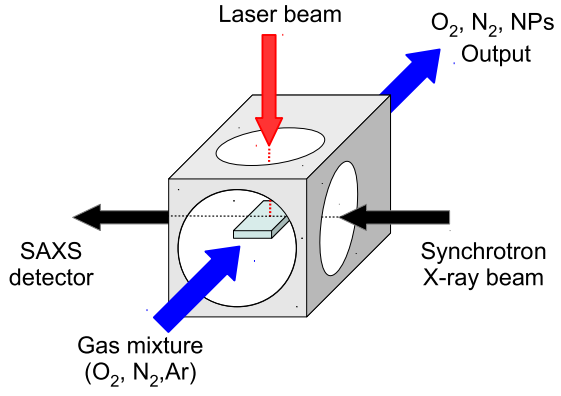

Fig. 1. Schematic view of the chamber devoted to laser treatments under a controlled atmosphere and in situ synchrotron scattering experiments.

The X-ray synchrotron beam (80 μm high and 300 μm wide) passed through the chamber in a fixed direction, perpendicularly to the laser beam, 600 or 800 μm above the target surface (for Ti and Al, respectively) in order to probe the plasma plume. Mica windows were used to allow passage into and out of the chamber. The energy of the X-rays was chosen to be 12 keV to reduce absorption by the ambient air and the detector was placed 4 m away from the target plume. In this configuration, the measured scattering vector, $q = (4\pi/\lambda)sin(\theta/2)$, where λ and θ are the wavelength of the incident X-ray radiation and the scattering angle, respectively, covers the range from 0.0022 to 0.2 Å^{-1} though in practice the upper limit is dominated by air scattering above 0.1 Å^{-1}. Since the particle size can be estimated to be $D \sim \pi/q$, NPs with sizes in the 3–140 nm range could be detected.

The preformed gas mixtures (or common air) were sent through the chamber during the SAXS experiments with a flow rate of 1 l/min. At the end of each run, the chamber was pumped to evacuate the gas and to avoid any NPs depositing on the target surface. Taking into account the gas flow in the chamber, a time of 50 μs between successive laser pulses and a duration of the plasma plume for a pulse roughly estimated in the microsecond range, the overalp of NPs formed by successive pulses can be neglected here. Measurements were made at different heights above the target surface but no significant difference in the NPs size was found.

The nanopowders formed during the pulsed laser irradiation of the targets in air could be collected and studied ex situ using conventional TEM, XRD and micro-Raman spectroscopy. The TEM set-up was a 200 kV JEOL 2100 (LaB_6) microscope. XRD patterns were recorded on a Siemens D5005 diffractometer using Cu Kα radiation. Raman spectra were obtained in back-scattering configuration using an InVia Renishaw set-up. The excitation wavelength was 532 nm and the excitation power focused on the sample was about 55 μW to avoid heating the samples.

3. Results and discussion

3.1. In situ SAXS studies

Analysis of the scattering pattern was performed using the single level Beaucage unified exponential/power-law fitting function [18]:

$$I(q) = G\exp\left(-\frac{q^2R_g^2}{3}\right) + B\left\{q^{-1}\left[\mathrm{erf}\left(\frac{qR_g}{\sqrt{6}}\right)\right]^3\right\}^P \quad (1)$$

which has a Guinier exponential form at low q and an associated power-law in the so-called Porod, high q region. R_g denotes the radius of gyration. G, B and P are the Guinier pre-factor, a surface area specific factor and the power-law exponent, respectively. To fit Eq. (1) to our data, the Small Angle Scattering (SAS) macro package from J. Ilavsky of the Advanced Photon Source has been used [19]. In the present case, all the background subtracted, scattered X-ray intensities were successfully fitted using a one-level function. Typical experimental data and the corresponding fitted curve are shown in Fig. 2.

In the SAXS measurements we were not able to see a Guinier region at low q but the TEM images taken ex situ (see below) show that the primary particles are agglomerated into much larger structures. Indeed the slope of the data at low q in Fig. 2 is on the order of 1 which is consistent with a chain structure.

Please cite this article in press as: M. Girault, et al., Influence of the reactive atmosphere on the formation of nanoparticles in the plasma plume induced by nanosecond pulsed laser irradiation of metallic targets at atmospheric pressure and high repetition rate, Appl. Surf. Sci. (2015), http://dx.doi.org/10.1016/j.apsusc.2015.10.090