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Microstructural analyses of the nanoparticles obtained after laser irradiation of Ti and W in ethanol

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Abstract

The laser ablation technique has been employed to prepare titanium (Ti) and tungsten (W) colloids from the elemental solids in ethanol using a copper-hydrogen bromide (CuHBr) vapour laser. The obtained nanoparticles were spherical with most diameters ranging from 0.05 to 0.5 μm. Some particles, notably when using Ti targets, are bigger than 0.9 μm, indicating resolidification of liquid droplets. The mechanism of material removal was characterized by photo-ablation where some particles were generated by rapid solidification from the melt. The W particles had tendency to coalescence, since small clusters merge to larger spheres. On the other hand, the Ti particles were coalescence-free, perhaps due to the thin high-resistant oxide layer at their surface.

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Keywords: Nanomaterials; Nanoparticles; Laser; Colloids

1. Introduction

Recently, laser ablation in liquids have attracted much attention as a new technique for materials processing, such as colloidal synthesis. It has been demonstrated that stable colloids containing nanosized metal particles are prepared by laser ablation of metal targets in liquid solutions [1–4]. In fact, these particles have shown very promising applications such as lubricants [5] and magnetic record media [6]. Advantages of the laser technique are the easiness of the preparation, speed and absence of chemical reagents in solution, in comparison with wet chemistry. Laser ablation of solids in liquid medium occurs when a high-power laser beam is focused at the submerged target surface for an appropriate time. The machining operation leads to the ejection of particles to the liquid where they are condensed and cooled. Molecular dynamics simulations [7] have proposed two different mechanisms of particle removal during ablation: below a given fluence threshold, there is desorption that is characterized by events in which primary individual atoms desorb. Above this threshold, the ejected plume contains a substantial fraction of large atomic clusters.

Two metal systems are studied here, tungsten (W) and titanium (Ti), aiming to produce nanoparticles for enhancement of mechanical properties of metallic alloys, such as steel, aluminum and titanium. The nanoparticles could be used for dispersion strengthening in a metallic matrix. Dispersion strengthening is a metallurgical process to promote hardening of a soft matrix through a discontinuous fine dispersion of a hard phase that interferes with dislocation slipping [8]. Another possibility belongs to carburized products (TiC and WC), which can be used in cobalt-cemented carbide hard metal articles for machining operations [9].

2. Experimental

A homemade copper-hydrogen bromide (CuHBr) vapour laser [10], has been used to produce surface ablation in a number of systems. This laser produces a very-high quality beam ($M^2 = 5$) that is particularly suitable for tungsten ablation as presented elsewhere [11]. The laser has a maximum average power of 22 W, typical pulse length of 30 ns and pulsing frequency of 13,000 Hz. The laser wavelengths are 510 nm

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(green) and 578 nm (yellow), with approximately 2:1 ratio between green and yellow intensities. The beam is mirrored into the solution through a lens with 100 mm focal length (spot diameter about 50 μm). The laser intensity at the focus position was approximately 3×10^9 W cm^{-2}. The laser beam strikes the surface horizontally after passing throughout a glass window and the liquid. Fig. 1a shows the crucible containing the liquid, the metallic target griped by tweezers, and the laser beam crossing the liquid. Fig. 1b presents a schematic view of the experimental set-up. To avoid the formation of deep holes, the metal plate was displaced under the laser beam with the help of a manual linear stage. The target metals were high-purity tungsten or titanium plates with dimensions 15 mm × 15 mm × 1 mm. Liquid medium was analytical purity ethanol, which is proved to be effective to minimize oxidation during laser ablation of metallic solids in liquids [12]. The processing time is 30 min for each run. In order to avoid contamination and further oxidation of the particles, the analyses were carried out immediately after the laser processing.

The collected colloids were analysed by optical absorbance, transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The absorbance spectra were measured by a Perkin-Elmer Lambda 20 spectrometer in transmission mode. The absorbance is the difference between the transmission spectra of the pure ethanol and the colloidal solutions. Here, the scattering is considered negligible because the particle density in the liquid is very low [13]. Transmission electron microscopy was carried out in a JEOL 200 C with 200 kV. TEM analyses were carried out using a drop of the colloid onto a copper mesh coated with an amorphous carbon film, which was then dried in a vacuum disiccator. Scanning electron microscopy was carried out in a JSM 5900 LV equipment. SEM micrographies are obtained from various drops of the colloid onto a mica substrate, which was dried inside the SEM chamber (low-vacuum mode).

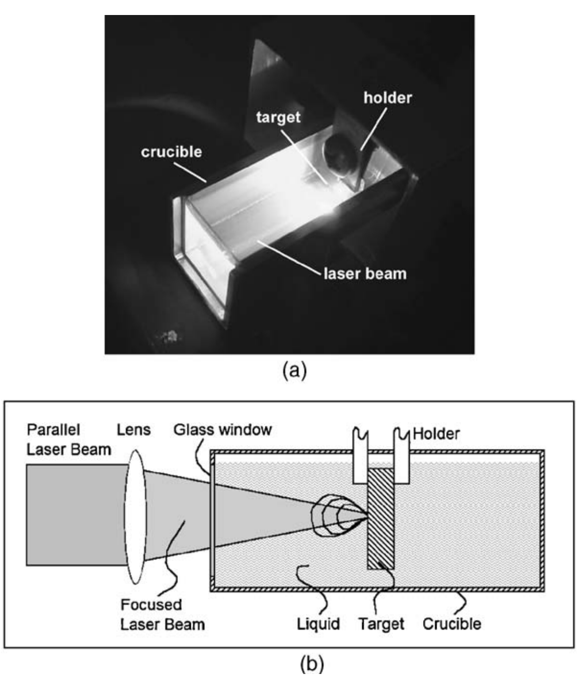

Fig. 1. (a) Experimental set-up. (b) Schematic presentation.

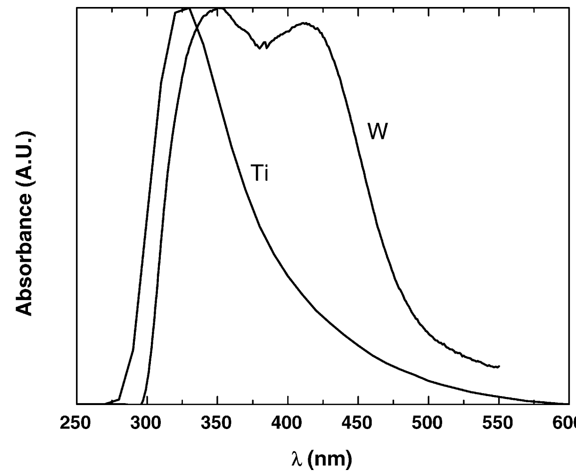

Fig. 2. Absorbance spectra of Ti and W particles produced by laser ablation.

3. Results

Fig. 2 shows the absorbance spectra of the ethanol solutions with Ti and W after laser irradiation. The spectra exhibit different shapes for Ti and W, with a relatively sharp peak at 325 nm for Ti and a doublet for W centred at 350 and 420 nm. The absorbance intensity is presented in arbitrary units because its scale depends on the particle concentration in the liquid.

Transmission electron images of the Ti and W nanoparticles are presented in Figs. 3 and 4, respectively. As could be seen, the micrographs show similar particle size distributions. Any clustering of nanoparticles is visible under this magnification, however, a closer view of the larger particles shows some satellites around them (Fig. 5).

Scanning electron images present a large particle size distribution. Figs. 6 and 7 show electron micrographs of W in

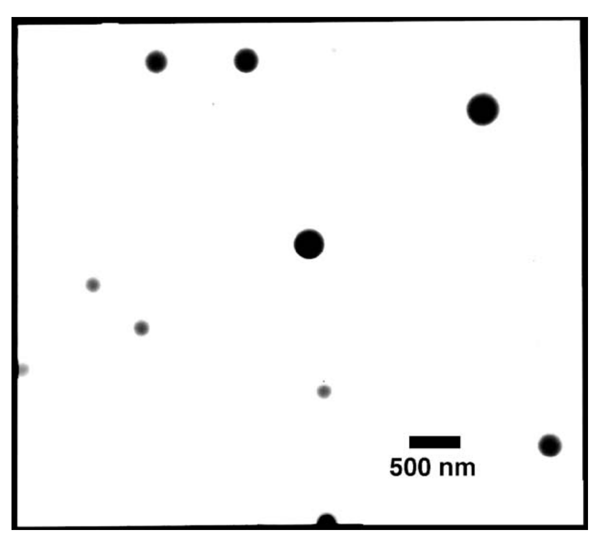

Fig. 3. Transmission electron microscopy of the Ti particles.