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Femtosecond pulsed laser ablation of molybdenum carbide: Nanoparticles and thin film characteristics

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ABSTRACT

In this paper we have used pulsed laser deposition (PLD) technique to ablate a Mo_2C target in vacuum by using an ultra-short pulse laser, with a 250 fs pulse duration, carrying out the study of both plasma and film characteristics. The aim of the work is to connect the film structure and morphology to the characteristics of the nanoparticles found in the plasma produced by the target ablation. To analyze the plasma we have used ICCD fast imaging and optical emission spectroscopy while the films have been characterized by X-ray diffraction, scanning electron microscopy and atomic force spectroscopy. The obtained results have been interpreted considering an ablation model which justifies the emission of molten nanoparticles directly from the target.

1. Introduction

Molybdenum carbide (Mo_2C) is a compound widely used in industrial applications, such as auto-motive piston rings, aero turbine engines and, in general as refractory and scuffing resistant coating material [1,2]. In addition, this carbide, like other transition metal carbides, including tungsten carbides, seems to be a promising material for proton exchange membrane fuel cells (PEMFCs) [3]. The slow kinetics at the cathode for oxygen reduction reaction (ORR) is considered as one of the major problems in PEMFCs development, and one strategy to increase the activity of ORR, and to decrease the catalysts cost or platinum loading, should be to explore new types of support materials. In fact, these materials play an important role in the dispersion of platinum nanoparticles and facilitate the transportation of reactants/products, which directly improve the catalytic activity and stability of catalysts. From this point of view, nanostructured molybdenum carbide films, as electro catalysts or their supports, could have an important promotion effect for ORR in PEMFCs, due to their interactions with Pt and their reactivity toward the hydrogen peroxide intermediate.

Among the different methods utilized for thin films deposition, pulsed laser deposition (PLD), performed by ultra-short laser pulses, has already shown itself to be a suitable technique to deposit nanostructured good quality films of refractory materials, in particular carbides [4–6] and borides [7–10].

In this paper we have studied the deposition of molybdenum carbide thin films by ultra-short PLD technique. The plasma produced by the laser–matter interaction has been analyzed by ICCD fast imaging and optical emission spectroscopy. These pieces of information have been used to clarify the ablation-deposition mechanism and, consequently, to improve the films characteristics. The deposited films, which resulted to be nanostructured, have been characterized by scanning electron microscopy, atomic force microscopy and X-ray diffraction. The results have been discussed in terms of a model considering the direct ejection of nanoparticles from the ablated target.

2. Experimental

The ablation and deposition experiments were performed by using the experimental apparatus previously described [4].

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It consists of a stainless steel vacuum chamber, evacuated to a pressure of 1.5×10^{-4} Pa, equipped with rotating target and substrate holder. The substrate holder can be heated up to 600 °C. A Light Conversion frequency doubled Nd:glass laser (527 nm emission wavelength, 250 fs pulse duration, 10 Hz repetition rate) was used for the ablation and deposition experiments. The laser fluence was 3.0 J cm^{-2} and the laser beam was incident at an angle of 45° on the target surface. The ablation target were hot pressed Mo_2C pellets from MANA while the deposition substrates were (1 0 0) oriented silicon from Cerac. The distance between the target and the substrate was kept at 2.5 cm and the films were deposited at three different temperatures (25, 300 and 600 °C).

Optical emission spectroscopy (OES) was carried out by a Princeton ICCD device (1024×1024 pixels). The width of the entrance spectrograph slit was 80 μm and the gratings employed were 1200 and 150 grooves/mm. The gated system had best time resolution of 2 ns and each acquisition was integrated with 50 laser shots in order to increase the signal to noise ratio. Varying the position of the optical elements by a micrometric translation stage, it was possible to obtain space-resolved emission spectra at different distances from the ablated target surface. The same ICCD system, equipped with a 105/35 mm quartz Nikkor lens, was used for acquiring 10 ns gated images of the lateral view of the overall plasma plume emission, in the range 200–800 nm. The acquisition was performed both by single shot and by accumulating up to 20 shots. The spatial resolution achieved by this system was 37 μm. Both ICCD fast imaging and time-resolved spectra were accomplished by delaying the data acquisition of the plasma emission in the range of 10–200,000 ns with respect to the laser pulse. In all cases every data acquisition was carried out on a not previously irradiated surface.

The structure of the films were evaluated by X-ray diffraction (XRD), utilizing a Philips X'Pert PRO using Cu Kα_1 radiation. The deposits morphology was studied by Atomic Force Microscopy (AFM–Park XE 120) and by a scanning electron microscopy (SEM) apparatus (Philips-FEI ESEM XL30).

3. Results and discussion

The plasma produced by the ablation of the Mo_2C target shows all the features already found for other systems ablated in the same experimental conditions and, in particular, the presence of both primary and secondary plumes [4–6]. OES reveals the presence, in the primary plume, of Mo I and C II emissions. The absence of emissions relative to neutral carbon is probably due to either the low intensity of the corresponding peaks or the high carbon ionization degree, as already seen for WC [6]. The values corresponding to the maxima of the velocity distribution curves for the different species are 2.5×10^6 cm s^{-1} for Mo I and 7.0×10^6 cm s^{-1} for C II.

The data from ICCD imaging show that the intensity of the primary plume is not very strong, and that this plume develops in the first microsecond after the laser pulse, with a front velocity of 2.0×10^6 cm s^{-1}. The value of the front velocity obtained in this case, comparable with those found for other carbides (2.5×10^6 cm s^{-1} in the case of TaC [11] and 1.0×10^6 cm s^{-1} in the case of VC [4]), is in good agreement with the velocity value obtained by OES for Mo I species. This result confirms that the images obtained by ICCD imaging are mainly due to the neutral molybdenum emission. In fact, the front velocity has been calculated on a time interval of 500 ns, while the signals corresponding to C II are detected only within the first 100 ns. The angular distribution of the primary plume, obtained considering the cosine exponent q in the expression $I(\theta) = I_0 \cos^q\theta$, where ($I(\theta)$ is the flux intensity along a direction forming an angle θ with the normal to the target surface and I_0 is the intensity corresponding to $\theta = 0$), is 4.3.

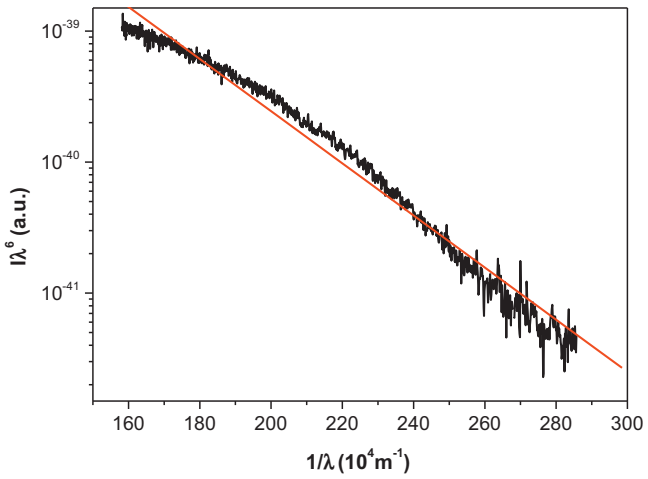

Fig. 1. Fitting of the secondary plume emission spectrum, recorded 1.0 μs after the laser pulse, at a distance of 0.1 mm from the target. The laser fluence was 5.0 J cm^{-2}.

After the quenching of the primary plume, a secondary emission of material can be observed. This secondary plume, which shows a low intensity, has a front velocity, calculated by ICCD imaging, of 3×10^4 cm s^{-1} and lasts about 20 μs. OES spectra achieved in this temporal regime, show black body like emission, suggesting the presence of hot particulates. By the same ICCD images, the cosine exponent for the secondary plume is 3.2. These values are very similar to those obtained for the carbide of another element of group 6, tungsten carbide [6].

In order to determine the temperature of the secondary plume, from the black body like emission, we have used the Wien's equation in the form: $I_\lambda \propto \varepsilon \frac{1}{\lambda^5} e^{-hc/\lambda k_B T}$, where I_λ is the radiation intensity, ε is the particle emissivity, λ the wavelength, T the temperature and k the Boltzmann constant. Taking into account that our apparatus measures photons and that, in the Mie approximation [12] $\varepsilon \propto 1/\lambda^x$, the Wien equation results $I_\lambda \propto (1/\lambda^{4+x}) e^{-hc/\lambda kT}$. There are no literature data about the dependence of ε from λ for molybdenum carbides, i.e. the value of x, but considering that for carbon x varies from 1.1 to 1.5 [13,14], while for many metals the same parameter presents a value varying between 1.5 and 2.0 [13], a value of $x = 2.0$, which corresponds to best linear fitting of the above equation, has been used. We have obtained an initial temperature of 3100 ± 100 K but, due to the low emission intensity, it has been impossible to determine its time evolution. Fig. 1 reports the fitting of the secondary plume emission spectrum, recorded 1.0 μs after the laser pulse, at a distance of 0.1 mm from the target.

Considering that the gaseous phase is very similar to those of the other transition metal carbides, it is not surprising that the deposited films also show the same characteristics already found in carbides deposited by ultra-short PLD. In fact, SEM micrographs show that the films are formed by a large number of particles with diameters apparently ranging from few nanometers to some hundreds of nanometers, as already seen for many systems deposited by ultra-short PLD [4–6,11]. In Fig. 2 the SEM image of a film deposited at a temperature of 300 °C is shown. The films morphology does not change by changing the substrate temperature. AFM measurements have been used to study both the first steps of the film formation and the particles size distribution. Fig. 3 shows the AFM image of the material deposited at room temperature with a very short deposition time (10 min), while Fig. 4 shows (a) the size distribution of the particles obtained by analysis of the same AFM and (b) the log-normal distribution of the particles diameters. From this graph we have obtained a particle average diameter of 80 nm.

XRD analyses, carried out on the different films, have shown, in those deposited at 600 °C, the presence of crystalline β-Mo_2C,