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Morphology and composition on Al surface irradiated by femtosecond laser pulses

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ABSTRACT

We study the surface chemicals and structures of aluminum plates irradiated by scanning femtosecond laser pulses in air for a wide range of laser fluence from 0.38 to 33.6 J/cm^2. X-ray photoelectron spectroscopy and X-ray diffraction analyses indicate clearly that crystalline anorthic $Al(OH)_3$ is formed under femtosecond laser pulse irradiation. Besides aluminum hydroxide, crystalline αAl_2O_3 is also found in the samples irradiated at high laser fluence. Field emission scanning electron microscopy demonstrates that the surfaces of the samples irradiated with low laser fluence are colloidal-like and that nanoparticles with a few nanometers in size are embedded in glue-like substances. For high laser fluence irradiated samples, the surfaces are highly porous and covered by nanoparticles with uniform size of less than 20 nm.

1. Introduction

The surface structuring on metals with femtosecond lasers has been researched increasingly in the recent years due to wide potential applications [1–7]. Surface structures present metals with interesting novel properties, such as enhanced light absorption and emission [8–11], increased photoelectron emission [12], superhydrophobic surfaces [13,14], and enhanced surface plasmon for chemical and biological applications [15]. In those researches, most experiments are performed in air and the interest has mainly focused on the varied structures induced by ultrashort laser pulses. When metals are heated by laser pulses in air, it is not very clearly how this provided oxidation environment affects on metal surface. Take aluminum as an example, which is most concerned due to its wide applications, it is well known that aluminum is easy-oxide and its clean surface will be covered with a thin amorphous aluminum oxide film about several nanometers thick when exposed to air in several picoseconds. When the femtosecond laser irradiates the aluminum surface in air, it is unclear how the surface chemical components and structures develop and the basic knowledge of metal surface is very important to its applications since the material surface always has a dramatic effect on its electrical, optical, chemical, and mechanical behavior. In this work, the aluminum plates are scanning irradiated by femtosecond laser under different fluences. The surface chemical and structure are analyzed. This research not only provides an explanation for property changes due to irradiation on aluminum surface with femtosecond laser but also develops a promising method for preparing nanoparticles with high porousness for ceramic applications [16].

2. Experimental

An amplified Ti:sapphire femtosecond laser system is employed to provide laser pulses with duration of 50 fs and central wavelength of 800 nm. The laser pulse has a Gaussian spatial profile and its repetition frequency is 10 Hz. An aluminum sheet with purity 99.99% and thickness 1 mm is cleaved into 10 mm × 10 mm plates. Before experiments, aluminum plates are mechanically polished and then ultrasonically cleaned with acetone, alcohol and water. After blown drying with nitrogen gas, the plates are put on the stage of a high precision computer controlled three-dimensional

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Table 1
Surface element contents calculated from XPS survey spectra in Fig. 1.

Laser fluence (J/cm^2)	Carbon	Oxygen	Aluminum	Nitrogen
Untreated	62.0%	28.7%	8.4%	0.9%
0.38	53.3%	35.4%	10.9%	0.4%
3.80	48.6%	38.2%	13.0%	0.2%
33.60	30.4%	52.6%	15.7%	1.3%

electrical translation (Newport). The laser beam is focused in air normally onto the surfaces of samples and the focal spot size is about 100 μm in diameter. The experiments are carried out to produce an extended area of surface structures by translating the samples relatively to the stationary laser beam along the horizontal direction followed by a vertical shift. The scanning speed is 0.1 mm/s and the vertical shift step is 50 μm. The incident laser energy is adjusted by using neutral density filters and the corresponding fluence on samples is varied from 0.3 J/cm^2 to more than 30 J/cm^2. After irradiation, the X-ray photoelectron spectra (XPS) are measured with ESCALAB 250 produced by Thermo-VG Scientific with an Al Kα (1486.6 eV) X-ray source. The X-ray in XPS measurement is focused on the sample surface with the diameter about 200 μm. Surface structures are analyzed on a theta theta rotating anode X-ray diffractometer (Rigaku D/maX-TTRIII, Japan) with an in-plane mode. Surface morphology is observed with a FEI Sivion200 field emission scanning electron microscope (EESEM).

3. Results and discussion

The XPS survey spectra of samples under different laser fluences are given in Fig. 1, compared with the untreated aluminum surface. All XPS spectra exhibit peaks originating from ejection of Al 2p, Al 2s, O 1s, O 2s, C 1s and N 1s core electrons and the atomic percent of each element calculated from its peak intensity is summarized in Table 1. Although N 1s peaks are not so obvious in XPS survey spectra due to the low content of nitrogen element, it is confirmed by its high-resolution scan spectra in Fig. 2.

Fig. 3 shows high-resolution scans of the Al 2p region. For untreated aluminum surface, besides a metallic Al peak at 71.7 eV BE, an oxidized Al peak at 74.5 eV BE from the natural oxide-film is also detected. The thickness d of this natural film can be calculated from the ratio I_o/I_m, the oxidic (o) and metallic (m) total primary zero-loss photoelectron intensities of the Al 2p main peaks, and is

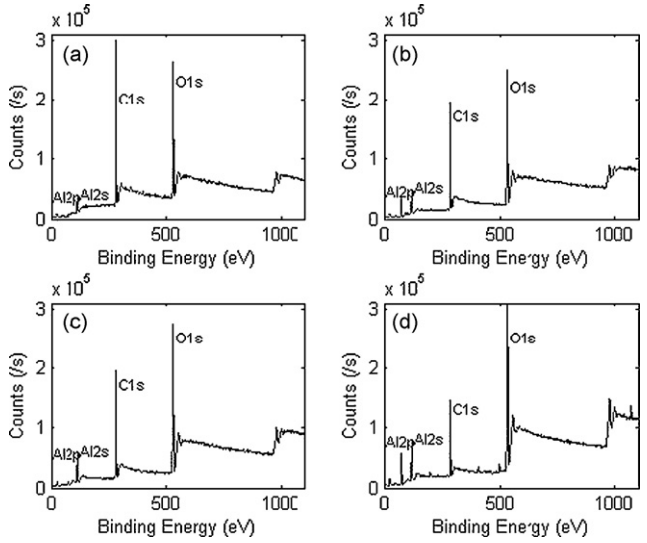

Fig. 1. XPS survey spectra of Al surface under different laser fluences compared with untreated Al surface: (a) without irradiation; (b) fluence 0.38 J/cm^2; (c) fluence 3.8 J/cm^2; (d) fluence 33.6 J/cm^2.

expressed as [17]

$$d = \lambda_o \sin\theta \ln\left[\frac{C_m\lambda_m}{C_o\lambda_o}\cdot\frac{I_o}{I_m}+1\right] \quad (1)$$

where λ_o and λ_m denote the inelastic mean free path of the analyzed photoelectrons propagating through the metal and oxide, respectively. C_m and C_o represent the volume densities of metal atoms in the metal and oxide and are taken as 100.14 and 71.85 mol/dm^3. The natural oxide-film is then calculated to be 4.1 nm thick and this value is in good accordance with the known data (for example, see Ref. [18]). For laser ablated aluminum samples the Al 2p region scans establish the cermet character of aluminum surface, i.e. an oxidized Al peak at about 74.3 eV binding energy (BE) only exist and the oxidation is enhanced at high laser fluence, seen from higher intensities of peaks. This means that the irradiation increases the nature oxide-film thickness on aluminum surfaces and the oxide-film thickness should be more than 10 nm since the maximum penetration length of photoelectron in XPS measurement is 10 nm.

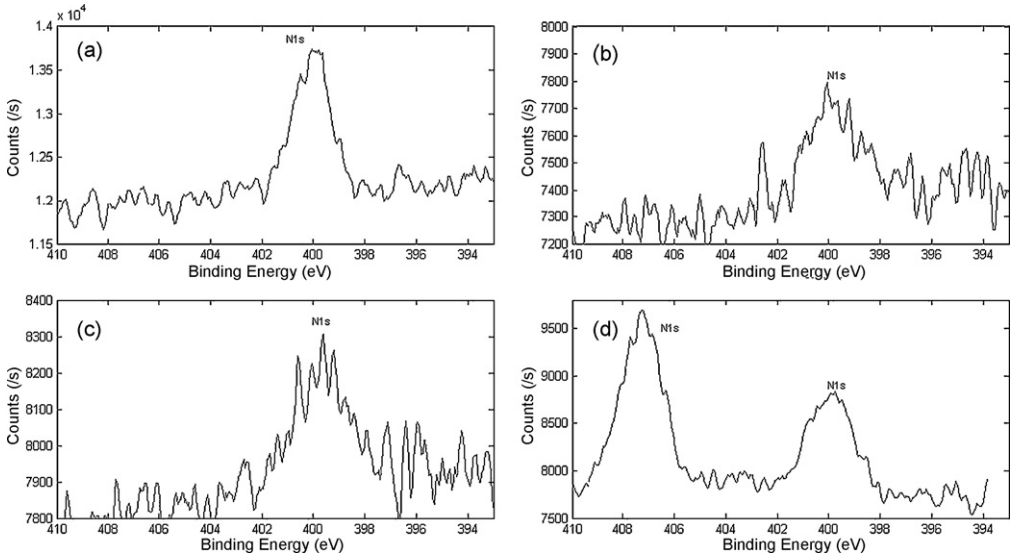

Fig. 2. High-resolution XPS spectra for N 1s: (a) without irradiation; (b) fluence 0.38 J/cm^2; (c) fluence 3.8 J/cm^2; (d) fluence 33.6 J/cm^2.