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Laser-induced surface alloying in nanosized Ni/Ti multilayer structures

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ABSTRACT

Laser-induced alloying effects on the composition and structure of different Ni/Ti multilayer structures were studied. Thin films composed of one, five, and ten (Ni/Ti) bilayers were deposited by DC ion sputtering on (1 0 0) Si wafers. Laser irradiations were performed by 150 ps pulses of a Nd:YAG laser operating at 1064 nm. The samples were characterized by Rutherford backscattering spectrometry (RBS), Auger electron spectroscopy (AES), X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM). At a laser fluence of 0.9 J cm^{-2}, interaction between Ni and Ti layers was initiated, and NiTi alloy formed in 5- and 10-bilayered samples. Progressed alloying was achieved at a laser fluence of 1.2 J cm^{-2}. The alloy was formed mostly within the heat affected zone (HAZ) of the sample. Surface segregation of titanium was followed by formation of a 25 nm thin TiO_2 film on the surface of the multilayered structures. In addition, parallel periodic surface structures on the surfaces of the 5- and 10-bilayered samples were clearly recorded. Their period in the case of the 5-bilayered system (0.77 μm) agrees very well with the predictions of the common theory, whereas, in the case of the 10-bilayered system, two periods of such structures are observed (1.43 μm and 0.4 μm), and none of them coincides with the prediction.

1. Introduction

Titanium-based alloys possess an attractive combination of low density, moderately high strength and good aqueous corrosion resistance for industrial and technological applications. Nickel–titanium (NiTi) alloys are one of the most important groups of structural materials in various modern industries. In fact, NiTi intermetallic compounds are competitive candidates for optical components in the field of soft X-ray and neutron optics, such as super mirror, polarizer, monochromator, etc. [1,2]. These alloys have been attracting great interest as powerful actuators in micromechanical systems (MEMS) such as microvalves [3], microfluid pumps [4] and micrograppers [5]. The nearly equal-atomic NiTi alloy as a relatively new biomaterial has attracted immense research interest because of its unique properties such as superelasticity, clamping capacity and shape memory effect [6–8]. However, metallic biomaterials have a tendency to corrode in a physiological environment, thereby accelerating the release of Ni ions which may cause toxic reactions in the body [9,10]. Quite an effective way to impede the leaching of nickel ions is to produce a barrier layer on the NiTi alloy by surface modification [11].

Among the various surface protection techniques, laser surface alloying is a relatively new technique that has been employed to improve hardness, wear, as well as corrosion resistance, and some other surface characteristics of both metallic and composite materials [12,13]. Laser processing of metallic surfaces is known to change material properties, such as material hardening or alloying of heterogeneous samples. During laser alloying, laser radiation as the heat source interacts with the material, and several complex phenomena such as melting, mixing of the components, alloy solidification and the resulting microstructure evolution have been observed. This technique has many advantages, as it allows rapid melting, intermixing and solidification in the alloyed zone, confined to a relatively shallow depth from the surface within a very short interaction time [14]. The process is characterized by extremely high heating/cooling rate (10^4–10^{10} Ks^{-1}), thermal gradient (10^5–10^8 Km^{-1}) and solidification velocity (1–30 ms^{-1}). The improvement of physical and mechanical properties of materials treated with laser radiation are associated with highly concentrated solid solutions, nanosized phases, intermetallic compounds, which are formed in surface layers [15]. The reason for synthesizing intermetallic compounds is that they belong to a unique class of materials which retain their structures up to their melting point and possess good mechanical properties. The intermetallic structures in the form of nanocrystalline states mainly possess good ductility and superplasticity even at low temperatures [16].

The present paper reports the results of an investigation on the possibility of NiTi intermetallic compounds formation by laser surface alloying. Different nanocomposite structures in the form of one, five, and ten (Ni/Ti) bilayer thin films on a Si substrate

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were irradiated by laser beam pulses in the picoseconds time domain. We investigated the effect of a 1064 nm picoseconds pulsed (Nd:YAG) laser on the composition and structural properties of different Ni/Ti multilayer systems. Multi-pulse action with a nonfocused beam and relatively low fluence was used to prevent ablation/evaporation of material in the irradiation areas. Our emphasis was to study the experimental irradiation conditions for the formation of NiTi intermetallic and oxide phases. In this experiment, multilayer structures are designed with a large difference in the number of layers and irradiated at constant laser parameters; in order to induce modifications at depths where intermetallic species formation is most probable.

2. Experimental

Nickel–titanium thin films in the form of different multilayer structures were deposited by d.c. sputtering of a water cooled, 99.9% pure Ni and Ti targets 6 cm in diameter by argon ions. The substrates on which the films were deposited were n-type silicon (1 0 0) wafers (0.5 mm thick), held at ground potential. They were cleaned by a standard HF etch and dipped in deionized water before mounting in the chamber. The deposition was carried out in a Balzers Sputtron II vacuum system. The conditions during the deposition process were: acceleration voltage and current 1.5 kV and 0.7 A, respectively. Base pressure was 1×10^{-3} Pa and partial pressure of argon 1.33×10^{-1} Pa. Prior to layer deposition, the substrate was additionally cleaned by backsputtering. Multilayer structures were deposited in a single vacuum run at $\sim$0.13 nm s^{-1} for Ni and $\sim$0.1 nm s^{-1} for Ti, without heating of the substrates. The deposited multilayer structures consisted of one, five, and ten (Ni/Ti) bilayers, with a total thickness of 40 nm, 160 nm, and 440 nm, respectively. The first layer deposited on the substrate was Ti and the outermost Ni.

In the experiment, the samples were irradiated by a nonfocused Nd:YAG laser beam (model EKSPLA SL212P). The irradiations of the different nanosized (Ni/Ti)/Si multilayer systems were performed in air, at a pressure of 1013 mbar and standard relative humidity. Due to high surface reflectivity of the target, the sample was placed so as to form an incidence angle of 22° with the laser beam. The laser output characteristics were: wavelength 1064 nm, pulse duration 150 ps, linear polarization. The pulse-to-pulse energy varied less than 5% and the pulse repetition rate was 10 Hz. The irradiations were done with 50 successive laser pulses at pulse energies of 65 and 85 mJ, at different distances between the sample and the laser, with fluences estimated to 0.9 J cm^{-2} and 1.2 J cm^{-2}, respectively. In order to obtain a sufficiently large irradiated area, necessary for Rutherford backscattering spectrometry and X-ray diffraction analysis, the samples were translated by 2 mm after each laser treatment. Thus were obtained irradiated areas of 20 mm × 3 mm. This ensured overlapping of the subsequent spots and the corresponding improved uniformity of the structures formed.

The diffuse reflectance spectra were recorded by a Labsphere RSA-PE-20, diffuse reflectance and transmittance accessory including an integrating sphere. The measurements were performed at a wavelength of 1064 nm, and $BaSO_4$ was used as the standard.

The phase composition and crystalline structure of the samples was studied by X-ray diffraction (XRD). Measurements were carried out on a standard Bruker D8 Diffractometer with parallel beam optics using Cu Kα diffraction patterns. Angle 2θ was scanned in the range from 30° to 60° at 0.02° steps, each 10 s. The RBS (Rutherford backscattering spectrometry) analysis was performed at the Microanalytical Center of the Jožef Stefan Institute in Ljubljana, Slovenia, using 4.53 MeV 7Li ions and a Si surface barrier detector, positioned at a scattering angle of 165°. All spectra were collected from 74.5° off normal incidence to the sample in IBM geometry. Detector resolution was 25 keV. The depth distribution of elements in the non-treated and laser treated areas of the 5×(Ni/Ti)/Si system was analyzed by Auger electron spectroscopy (AES) in a PHI SAM 545 spectrometer. For electron excitation a primary electron beam of 3 keV and 1 μA, with a diameter of 40 μm, was used. During depth profiling the samples were sputtered by two symmetrically inclined Ar ion beams of 1 keV at an ion incidence angle of 47° with respect to the surface normal. The sputtering rate was estimated to about of 1.2 nm min^{-1}, measured on a Ni/Cr reference structure of known thickness. The changes of surface morphology induced by laser irradiation were examined by atomic force microscopy (AFM, Solver PRO 47) and scanning electron microscopy (SEM, JSM 840A).

3. Results and discussion

The initial reflectivity measurements in the IR spectral region at 1.06 μm showed that the Ni/Ti multilayer structure had high initial reflectivity (ca.93%). As-deposited Ni/Ti multilayer samples possessed a typical silver–grey metallic color, while the surface was mirror-like. Microscopic methods have shown that the structure of the sample was highly homogeneous, with a low mean surface roughness of about 0.5 nm. Initial laser pulses change surface morphology and cause physico-chemical transformations. In the present experiment the laser pulse fluence of 0.9 J cm^{-2} induced a noticeable damage after 50 pulses, and the high reflectivity was lost with accumulating the pulses. The damage on the Ni/Ti multilayer thin film, after laser irradiation, was recognizable as a broad blurred area, visible to the naked eye. The initial reflectivity of the (Ni/Ti) sample falls sharply, so that after 50 pulses it reaches a value of about 71.8%. It is evident that the level of Ni/Ti multilayer modification can be significant after successive action of several tens of laser pulses.

The results of RBS analyses of different (Ni/Ti)/Si multilayer structures, before and after laser treatment with 50 successive pulses are shown in Fig. 1. Experimental spectra (Fig. 1a) were taken in IBM geometry from an as-deposited 1x(Ni/Ti)/Si sample and a sample irradiated by 50 laser pulses. The signals arising from Ni and Ti layers in as-deposited sample were well separated. Significant changes in the RBS spectrum were recorded after irradiation with 50 laser pulses (Fig. 1a). Signals for Ti and Ni disappeared in the RBS spectrum, but a new broad peak appeared, with a visible plateau. The broad peak indicates that intensive mixing occurred between the components of the individual Ni and Ti layers. The appearance of the plateau can be contributed to the formation of the NiTi intermetallic compound. The high-energy edge of the broad peak does not coincide with the corresponding edge of the Ni signal. This shift of the new peak to a lower energy signifies that the initial pure Ni is not present on the surface. In fact, nickel on the surface may be present in the form of a compound such as alloys or oxides (since the irradiation was done in air). On the other hand, the low-energy edge of the broad peak is shifted towards the Si signal, which can be attributed to the mixing of the thin film components with the Si substrate. Also, it can be noted that the Si signal is changed after laser modification. The intensity of the Si signal becomes lower near its high-energy edge, which is shifted to higher energies with the formation of the plateau. This result could mean that the laser induced production of silicide phases in the 1×(Ni/Ti)/Si system.

The sample of as-deposited multilayered 5×(Ni/Ti)/Si has shown clearly visible individual layers of Ni and Ti, although three layers of Ni and Ti overlap in the RBS spectrum (Fig. 1b). The signals corresponding to Ni were obscured by Ti signals, which are manifested by increased intensity of the three middle peaks. The RBS