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Surface modification of W-Ti coatings induced by TEA CO_2 laser beam

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Abstract

In this work, the interaction of a transversely excited atmospheric (TEA) CO_2 laser with tungsten–titanium (W-Ti) alloy deposited on austenitic stainless steel is considered. The W-Ti alloy as a refractory material possesses very good physicochemical characteristics such as thermochemical stability and high melting temperature. Studying of interactions of different energetic particles or laser beams with W-Ti coatings has both application and fundamental importance.

The morphological features of the W-Ti coating, deposited on austenitic stainless steel AISI 316, induced by a TEA CO_2 laser after multipulse cumulative laser action, have been considered. The laser pulses with tail (FWHM = 120 ns, tail = 2 μs) and free-tail pulses (FWHM = 80 ns) have been employed. Laser pulses used in the experiment had equal peak power density $I = 120$ MWcm^{-2}. For the given peak power density, excessive surface changes on the coating were registered. From direct observation on a microscopic scale (OM, SEM), it can be concluded that W-Ti coatings show different behavior under laser irradiation with various temporal pulse shapes.

1. INTRODUCTION

Surface modification studies of thin films/coatings induced by various types of energetic beams, including a laser beam, are of a great fundamental and technological interest. In this context it must be emphasized that investigations of the laser beam interaction with various coatings are highly interesting (Nenadovic, 1996). The interaction of a pulsed TEA CO_2 laser beam with a tungsten–titanium (W-Ti) alloy deposited on a metal substrate is insufficiently known in the literature.

Thin films and coatings of the system tungsten–titanium on different substrates have been developed as an alternative to titanium-based thin films/coatings, which are considered for broad applications. Because of their specific structural, electrical, mechanical and optical properties, tungsten–titanium thin films/coatings have many promising applications. They can be used as protective material—anticorrosion coating for increased oxidation resistance (Sangaletti *et al.*, 1987)—microelectronic coatings—diffusion barriers for decreased surface diffusion (Oparowski *et al.*, 1987)—and as gas sensors for the detection of pollutants (Di Gulio *et al.*, 1998).

The presence of the active element titanium in alloy reduces the accumulation of voids at the oxide/alloy interface and in that way causes the modification of the oxide microstructure of the surface. The addition of titanium to tungsten improves the corrosion resistance and increases the adhesion by interconnecting metal bands. Titanium also improves the diffusion barrier performance of tungsten owing to its affinity for nitrogen and oxygen (Ting & Wittmer, 1982).

The purpose of this work was to study the surface modification of W-Ti coatings with the TEA CO_2 laser, which emits infrared radiation at a wavelength of about 10 μm. Special attention was devoted to monitoring of the surface morphology modification as a function of the laser pulse shape.

2. EXPERIMENT

The coating was deposited onto steel substrate by d.c. sputtering of the tungsten–titanium alloy (90%W–10%Ti). Austenitic stainless steel AISI 316 samples used in the experiment were of the plate form, rectangular shape (dimensions 25 mm × 13 mm × 2 mm). Before deposition, the substrate was polished and cleaned. The sputter deposition was performed at room temperature using a BALZERS SPUTTRON II vacuum system. Acceleration voltage ($U =$ 1.5 kV) and current on target ($I = 0.7$ A) were maintained at

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a constant during the experiment. The base pressure in the chamber was $p = 1.33 \times 10^{-3}$ Pa and the partial pressure of argon was $p_{Ar} = 1.33 \times 10^{-1}$ Pa. Under such conditions, the constant deposition rate was 0.095 nms^{-1}. The thickness of W-Ti layer was 900 nm.

The phase composition and crystalline structure of W-Ti deposit was determined by the X-ray diffraction method (Cu $K\alpha$ emission). The X-ray spectra were obtained by a power diffractometer with Ni filtered emission. Angles 2θ in the range from 30° to 80° were scanned by a step of 0.02° 2θ in time sequences of 1 s.

Reflectivity characterization of the sample for a spectral region of 6.5 μm to 14 μm were carried out using a SPECORD 75 IR spectrophotometer.

The surface morphology and crystalline size of deposited W-Ti coating were analyzed by scanning tunneling microscopy (STM) at room temperature and under atmospheric pressure. The STM image was obtained in constant current mode using a Pt (10%)Ir tunneling tip. Grain size and surface roughness of the deposited W-Ti crystallite coating was measured using the section analysis program in STM.

Laser-induced surface modification was carried out by a pulsed, UV preionized TEA carbon dioxide laser. The laser operated with nontypical CO_2/X, $X = H_2$; H_2/N_2, for a difference from typical CO_2/Y, $Y =$ He; He/N_2 gas mixtures. The presence of hydrogen in the laser increased the efficiency of the system (Trtica & Ribnikar, 1989). It is well known (Hermann *et al.*, 1993) that the laser pulse shape can be controlled by adjusting the gas mixture content. The nitrogen-rich mixture gave a longer laser pulse and a pulse with a tail (A-type pulse) while its absence resulted in a tail-free pulse (B-type pulse). Characteristics of laser pulses are given in Table 1.

The laser has been running in a multimode regime. The beam cross section is typically of quadratic form, so that spatial-uniform distribution of intensity can be assumed (Lamberton & Roper, 1978). Detailed characteristics of the laser used in the experiment are presented in Table 1.

The tungsten–titanium coating irradiation was performed with a focused laser beam. KBr lens with focal length of 6.0 cm ensured focusing onto the target. The incidence angle of the laser beam in respect to the surface was 90°. The interaction was performed in air atmosphere, at a pressure of 1013 mbar and relative humidity of 60%.

After the laser irradiation of the W-Ti coating the change in surface morphology was monitored by optical microscopy (OM) and by scanning electron microscope (SEM) with secondary (SE) electrons detectors.

3. RESULTS AND DISCUSSION

Before the irradiation of tungsten–titanium coating deposited on steel, X-ray diffraction microstructure analyses has been carried out. The X-ray diffractogram of the coating as deposited presented in Figure 1a has shown diffraction lines which corresponded to the bcc α-tungsten phase. On the diffractogram mainly a (110) preferred growth orientation was found with the presence of (211) crystalline orientation which was less expressed. The obtained value for the W-Ti lattice parameter of a = 0.3224 nm compared with a value of α-tungsten of a = 0.3165 nm. It can be seen that the addition of the titanium to the W-layers resulted in an expanded α-tungsten lattice. It can be concluded that a coating of W (90%)–Ti (10%) alloy was a single-phase, two component system. The surface morphology of deposited W-Ti coating on austenitic stainless steel is presented in Fig-

Table 1. *The typical TEA CO_2 laser operational conditions during the irradiation experiment*

Parameters	A-pulse	B-pulse
Gas mixture	$CO_2/N_2/H_2$	CO_2/H_2
Content	1/2.1/1.3	1/1.3
Output pulse energy	to 200 mJ	to 36 mJ
FWHM[a]	120 ns (initial spike); ~2 μs—pulse tail	80 ns
Peak power	to 0.5 MW	to 0.45 MW
Mode structure[b]	Multimode output	
Beam divergence[c]	~10 mrad	
Laser cavity	Nondispersive	
Spectral composition[d]	Simultaneous two-lines operation in P-branch 00°1 → 10°0 vibrational band	
Pulse repetition rate	2 Hz	

[a] Full width at half maximum.
[b] The laser possesses a high multimode output. The unfocused laser beam has a quadratic cross section with dimensions 1 × 1 cm.
[c] This value is measured in relation to the near field.
[d] The laser simultaneously operates at two wavelengths, i.e., 10.5709 and 10.5909 μm, P(18) and P(20) transitions. P(20) transition is more intensive.

ure 1(b). The STM micrograph indicated that the deposit had the polycrystalline form with fine grain structure uniformly covering the substrate. The mean values for grain size and mean surface roughness were 111.6 nm and 5.119 nm.

Reflectivity measurements in the spectral region of about 10 μm have shown that W-Ti coating had initial reflectivity of 95% (Petrovic *et al.*, 2000). The W-Ti deposited on steel substrate reveals mirror reflection with a very small part of the diffusion scattering. It is well known that the reflectivity of a target surface depends on its quality, temperature, and number of previously accumulated pulses (Ursu *et al.*, 1991).

The surface modification of W-Ti coating was observed after 20 and 500 cumulative laser pulses. The induced morphological changes, showed their dependence on beam characteristics: pulse energy, laser pulse duration, peak power density, and number of pulses. The energy absorbed from the beam is converted into thermal energy, which generates a series of effects such as melting, vaporization of molten material, exfoliation, dissociation or ionization of the vaporized material, and shock waves in the vapor and in the solids.

For a tungsten–titanium coating on steel substrate, the damage threshold has been determined. It depended on beam characteristics and material properties, too. The threshold, defined as the minimum fluence that creates detectable damage of the W-Ti surface, is reached after 20 pulses (Gakovic *et al.*, 1999). For W-Ti coating on austenitic stainless steel AISI 316, it was determinated at 30.3 and 16.0 J/cm^2, depending whether the laser operates in the tail (A-type pulses) or tail-free pulse (B-type pulses) regime. The peak power density during these measurements was 70.0 and 120 MW/cm^2 for A and B laser pulse types, respectively.

Surface changes of tungsten–titanium coating in the irradiation zone, registered after 500 pulses, were more prominent than in the case of 20 pulses. The morphology features of the tungsten–titanium coating on austenitic stainless steel

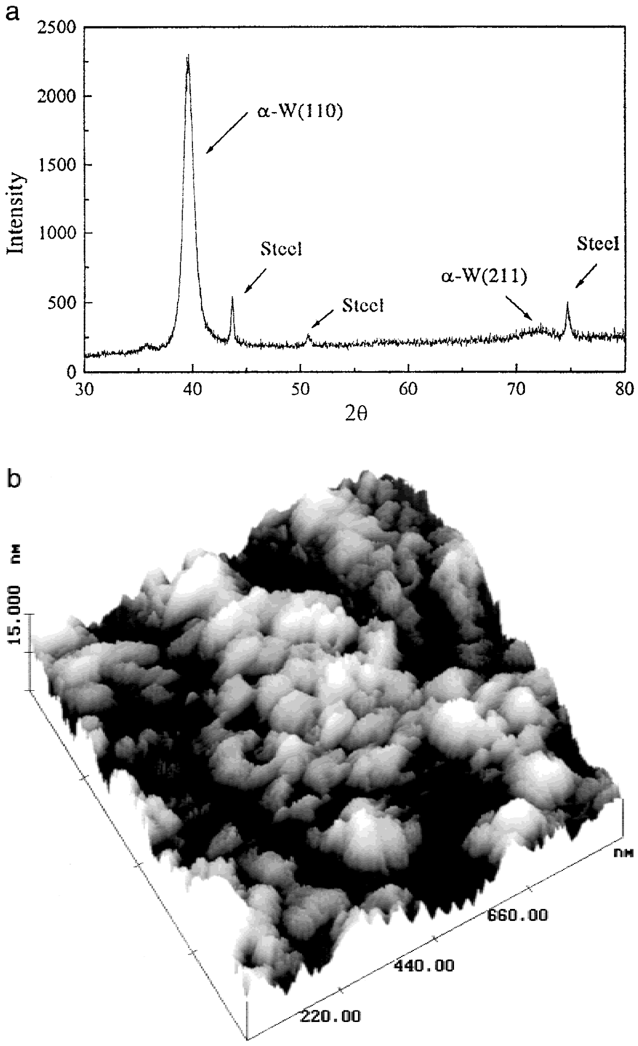

Fig. 1. Structural analysis of a deposited tungsten–titanium layer (thickness = 900 nm) on austenitic stainless steel AISI 316 substrate: (a) X-ray diffractogram and (b) STM micrographs (scan 880 nm × 880 nm).

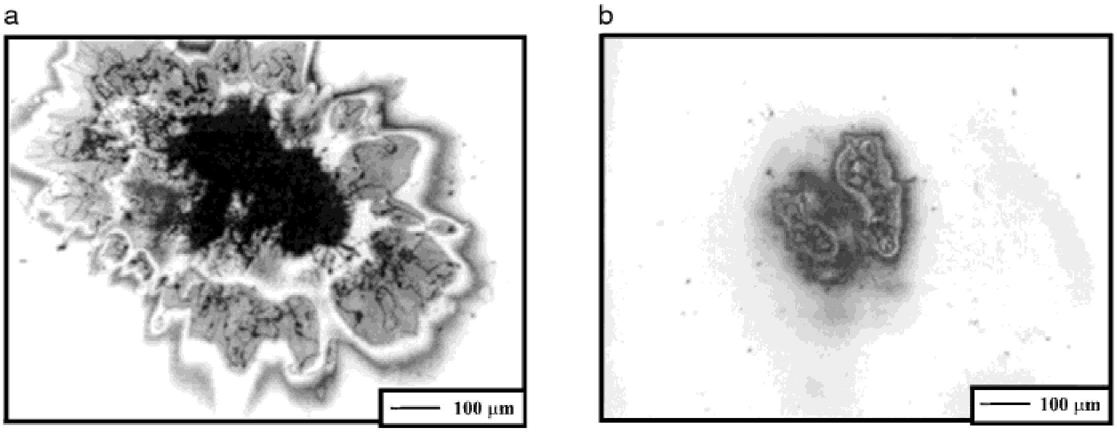

Fig. 2. The effect of TEA CO_2 laser radiation on tungsten–titanium coating deposited on austenitic stainless steel substrate. The cumulative action of 500 laser pulses is observed by optical microscope. (a) Pulse shape with tail—A type, (b) tail-free pulse shape—B type.

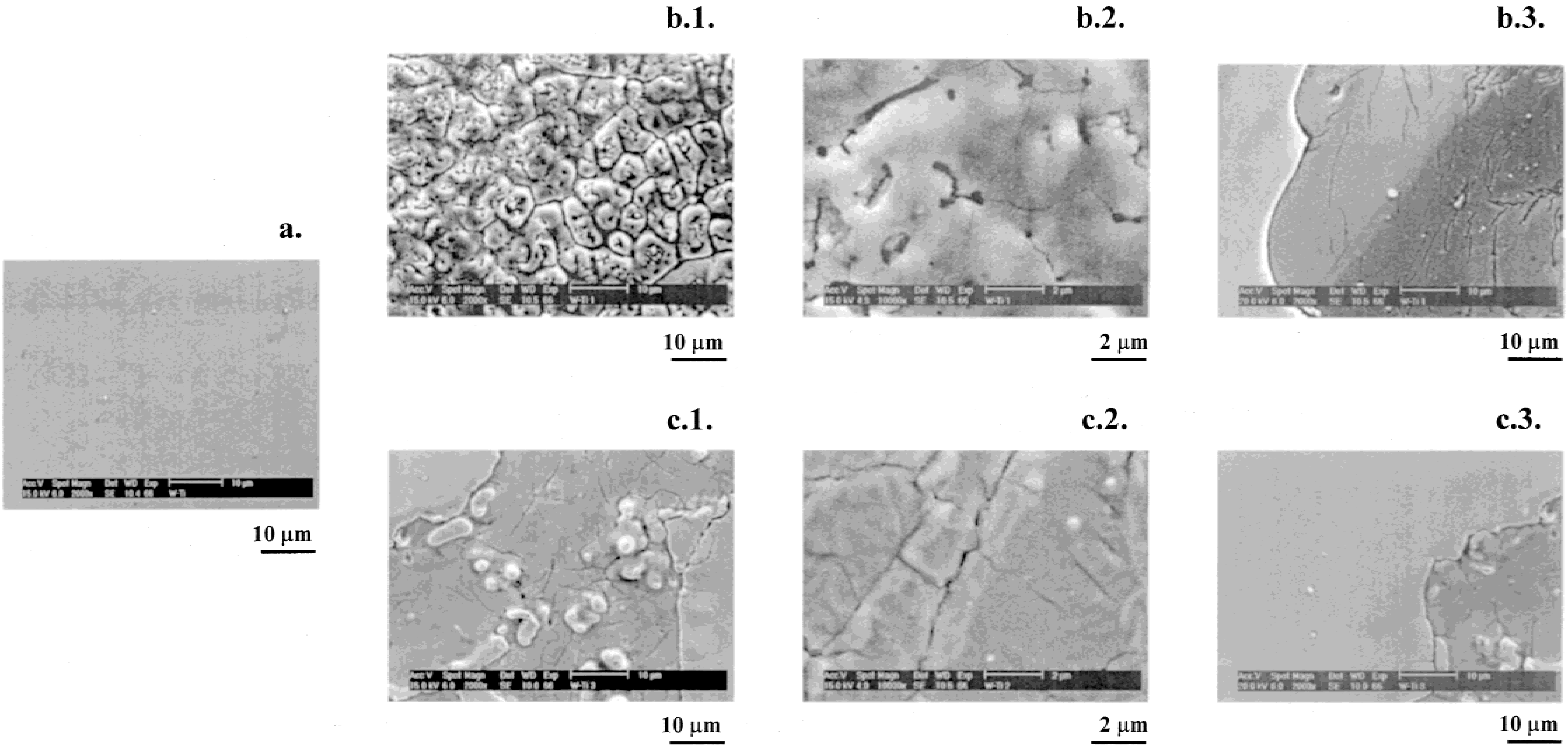

Fig. 3. The morphology of the tungsten–titanium coating on austenitic stainless steel substrate AISI 316 induced by TEA CO_2 laser. The analysis has been carried out by scanning electron microscope. (a) The tungsten–titanium coating before laser treatment. Changes induced after action of 500 cumulative laser pulses: (b) Action of A-pulse type. Deposited energy = 48 J/cm^2. In central zone (b.1. and b.2.) and at the periphery of the interaction (b.3.); (c) Action of B-pulse type. Deposited energy = 18 J/cm^2. In central zone (c.1. and c.2.) and at the periphery of the interaction (c.3).

substrate AISI 316 as a function of the laser pulse shape are presented in Figures 2 and 3.

The results show that the action of 500 laser pulses, at a peak power density of 120 MW/ cm^2, lead to the important changes of the tungsten–titanium coating. The changes on the macroplane are presented in Figure 2. After irradiation of W-Ti coating with A-type pulses, the damage area is clearly expressed in central part and broad periphery. The damage area induced with B-type pulses is not explicitly divided. The consequence of higher pulse duration in the case of the A-type pulse is an about three times greater relative damage area than for the B-type pulse.

Morphological characteristics have been analyzed in all investigated areas. Surface modifications, in details, can be presented as follows. The pulses with tail (A-type pulse) caused more evident morphology modification (Fig. 3b1 and b2) in comparison with tail-free pulse (Fig. 3c1 and c2). By comparing microphotographs obtained by means of OM and SEM analysis it can be concluded that exfoliation in the central zone appears during irradiation by both types of pulses. By irradiation of the A-type pulse, drastic topographic changes on the substrate are obtained (Fig. 3b1). After the multipulse action of tail-free pulses (B-type pulse), topographic changes on the substrate are less expressed as compared to the previous case. For both laser pulse types, a sharp border between coating and substrate (Fig. 3b3 and c3) can be seen, as a consequence of layer exfoliation. Hydrodynamical sputtering is not recorded.

4. CONCLUSION

The interaction of a pulsed TEA CO$_2$ laser with tungsten–titanium coating on austenitic stainless AISI 316 has been studied. Attention was paid to monitoring the laser-induced surface changes.

The obtained W-Ti coating has the polycrystalline form with fine grain structure uniformly covering the substrate. For the laser radiation used the W-Ti posesses a high value of reflection (95%). The surface modification of W-Ti coating was observed after 20 and 500 cumulative laser pulses. In this experiment the laser damage threshold for laser pulse type with different temporal shape was determined. The smaller damage threshold (peak power density of 70 MW/ cm^2) was obtained for pulse with tail (A pulse), than for the tail-free pulse (B pulse type; 120 MW/cm^2). For the same peak power density, the relative damaged area after 500 cumulative laser pulses with tail is three times greater than for the tail-free pulse. The layer exfoliation was observed for both laser pulse types.

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