Appl. Phys. A 79, 1353–1355 (2004)
DOI: 10.1007/s00339-004-2778-8

Applied Physics A
Materials Science & Processing

B. GAKOVIĆ[1,✉]
M. TRTICA[1]
P. PANJAN[2]
M. ČEKADA[2]

Surface modification of the Cr-based coatings by the pulsed TEA CO_2 laser

[1] Institute of Nuclear Sciences "Vinča", P.O. Box 522, 11001 Belgrade, Serbia, Serbia and Montenegro
[2] Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

Received: 15 September 2003/Accepted: 4 March 2004
Published online: 26 July 2004 •

ABSTRACT The interaction of a transversely excited atmospheric (TEA) CO_2 laser with chromium oxynitride (CrON) coating deposited on a AISI 304 steel substrate was considered. The results have shown that CrON was surface-modified by the laser beam of 45 J/cm^2 energy density. The energy absorbed from the TEA CO_2 laser beam was partially converted into thermal energy, which has generated a series of effects such as melting, vaporization of the molten material, and shock waves in the vapor and in the solid. Morphological manifestations on the CrON coating surface can be summarized as follows: non-uniform features with ablation and appearance of crater-like form (central zone of interaction); appearance of three damaged areas and presence of hydrodynamic effects with resolidified droplets (periphery zone of interaction). In case of applied energy density the interaction of laser radiation with CrON has been always followed by plasma creation in front of the coating.

PACS 79.20.Ds; 61.80.Ba

1 Introduction

Investigation of laser-induced surface modifications of solids, both in bulk and in thin film form, is important for understanding the physical mechanisms in the interaction processes as well as from the reason of the technological applications [1–4]. Generally, the morphological changes of the solid surface induced by the laser depend on the laser beam and target material characteristics [5]. Chromium based coatings have been investigated for over a decade and were successfully implemented in many areas. In this context, the following coatings can be mentioned [6]: CrN, CrC, CrCN, etc. Chromium based coatings exhibit excellent properties like high hardness, oxidation resistance, chemical stability, etc. [7]. Due to its high hardness and brittleness, mechanical micro structuring is extremely difficult, thus the laser beam treatment is one of possible solutions.

Morphology modifications of chromium oxynitride treated by the pulsed TEA CO_2 laser are the main topic of this paper. The coating was deposited on chromium that was used as an intermediate layer between AISI 304 steel substrate and the coating. No data have been found in the literature about experiments with laser pulse irradiation of chromium oxynitride coatings. At the same time, the results on surface modification of some nitride coatings, based on transition metal similar as chromium, can be found in literature [4, 8, 9].

✉ Fax: +381-11/3440100, E-mail: biljana.gakovic@physics.org

2 Experiment

Chromium oxynitride coatings of 3 microns thickness were deposited by plasma-beam sputtering technique in a Sputron (Balzers) apparatus. Details of the deposition procedure are described elsewhere [6, 7]. AISI 304 stainless steel of 15 mm in diameter and 1.5 mm in thickness was used as a substrate. Prior to deposition process, the substrate was polished using a standard metallographic procedure. A thin metallic layer, in this case Cr (thickness $= 0.5\,\mu$m), was initially deposited on steel to ensure good adhesion between CrON and substrate.

Laser induced surface modification was performed by the pulsed UV preionized TEA CO_2 laser. The laser output parameters can be found elsewhere [4, 10], but some of the characteristic parameters, essential for this experiment, will be mentioned here: pulse laser energy density (fluence F)- up to 45 J/cm^2; peak power density- up to 150 MW/cm^2; laser pulse temporal shape-FWHM of about 100 ns (initial spike) and a tail (added on spike) with length of about 2 μs; pulse repetition rate 2 Hz; mode regime-TEM_{00} mode; spectral output – about 10.6 μm; the typical gas mixture- $CO_2/N_2/He$. Multi-pulse laser irradiation (up to 400 pulses) of the coating was performed in air atmosphere. The surface of coating was placed perpendicular to the direction of incident laser beam in the focal plane of NaCl plan-convex lens (focal length = 6 cm).

Various analytical techniques were used for characterization of the coatings surface. The surface morphology was examined by optical microscope (OM) and by scanning electron microscope (SEM; JEOL-JXA). The profilometer (Taylor–Hobson Talysurf 2) served to measure surface roughness and topographic changes of irradiated surface region, i.e., the geometry of the ablated areas. The reflectivity of the coating, prior to laser action, was measured by an infrared spectrophotometer (SPECORD).

3 Results and discussion

The chromium oxynitride coating prepared by the sputtering technique exhibits a crystal structure corresponding to the face-centred cubic phase of a chromium nitride (CrN). The CrON coating exhibited a fine-grained microstructure with an average grain size less than 20 nm. The initially measured value of surface roughness was 10 nm. In general, the grain size and surface roughness have increased with coating thickness.

Investigation of the CrON morphological changes induced by laser radiation has shown their dependence on beam characteristics: primarily on the laser pulse energy density, peak power density, laser pulse duration, number of pulses, laser mode structure, etc. It is assumed that energy absorbed from the TEA CO_2 laser beam is converted into thermal energy, which generates a series of effects such as melting, vaporization of molten material, dissociation or ionization of vaporized material and shock waves in vapor and in the solid. It can be assumed that a relatively high temperature was reached over the surface and is probably responsible for CrON ablation. Temperature is in strong correlation with used laser intensity and target absorptivity [11], which is further in correlation to the reflectivity. Measured reflectivity value for chromium oxynitride coating, prior to laser irradiation, was of about 61% at wavelength of 10.6 μm corresponding to emission line of used TEA CO_2 laser. Relatively high absorptivity of the target implies that the coupling between laser radiation and target was efficient.

Surface variations in the irradiated zone, registered after 100 or 400 pulses, were more prominent than after 2 and 5 pulses. Morphological features of the CrON are presented, for low (2, 5) and high numbers (100, 400) accumulated laser pulses in Figs. 1 and 2. The action of the laser radiation when deposited energy density was 45.0 J/cm^2 causes significant surface modification of the CrON surface. In the central part of damaged area, micro-cracking was registered after two and five pulses action (Figs. 1B2 and 2A1), while ablation with the appearance of crater like form of the CrON coating was obtained after 100 and 400 pulses action (Figs. 1C1

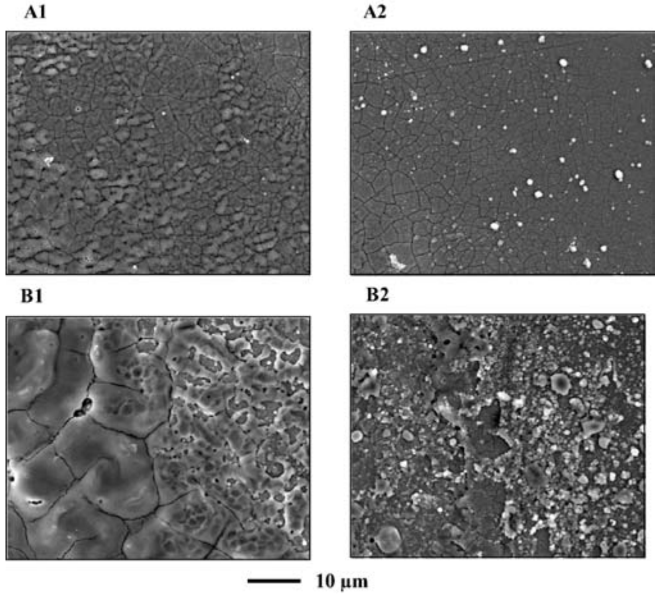

FIGURE 2 The view (registered by SEM) of CrON coating after TEA CO_2 laser irradiation. **A** – effects of five laser pulses (**A1** and **A2** – centre and periphery of the damaged area, respectively); **B** – effects of 400 laser pulses (**B1** and **B2** – centre and periphery of the damaged area, respectively) (TEM_{00} mode; $F = 45.0\,J/cm^2$)

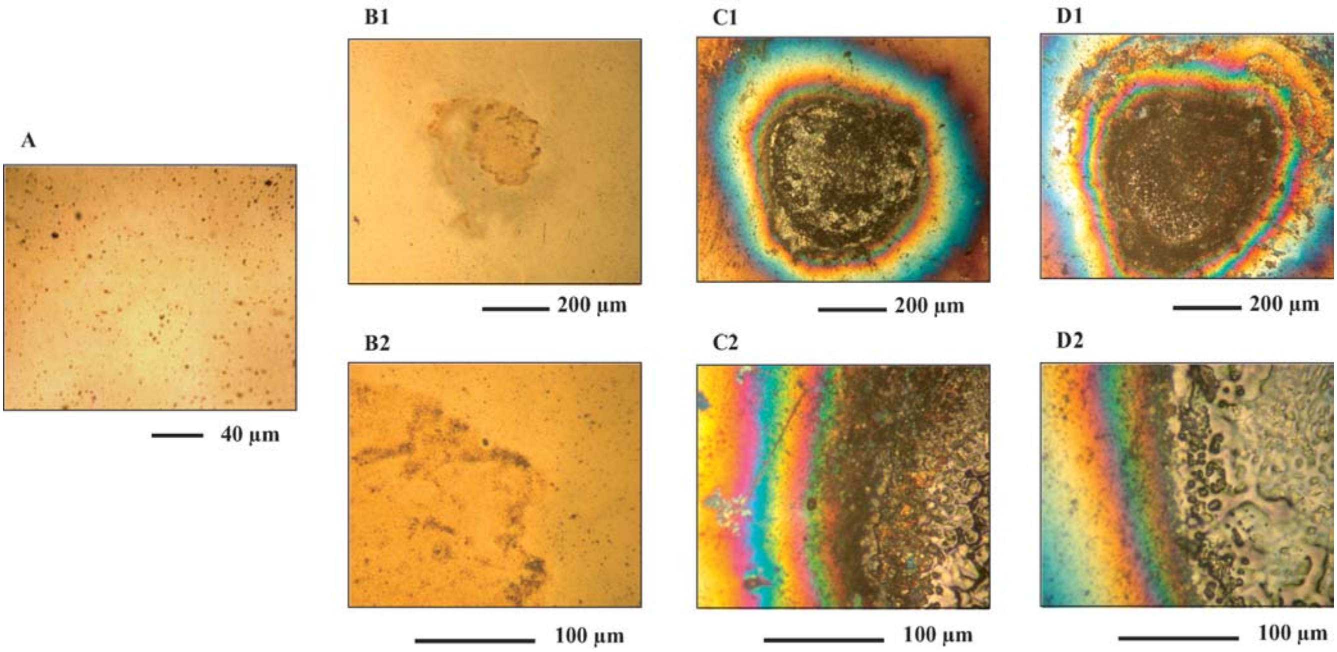

FIGURE 1 The view (registered by OM) of CrON coating prior to and after TEA CO_2 laser action. **A** – The CrON coating deposited on the AISI 304 steel substrate before laser irradiation. **B**, **C** and **D** – The view of the coating after laser irradiation (**B1**, **C1** and **D1** – entire spots after 2, 100 and 400 cumulative laser pulses, respectively; **B2**, **C2** and **D2** the centre and periphery of the damaged area after 2 and 100, 400 laser pulses, respectively) (TEM_{00} mode; $F = 45.0\,J/cm^2$)

and 1D1). In the periphery zone of the damage, after action of two and five accumulated pulses, hydro-dynamical effects are poorly visible (Figs. 1B2 and 2A2). Action of the 100 and 400 cumulated laser pulses (Figs. 1C, 1D and 2B) causes the following effects: (i) partial ablation of CrON coating with non-uniform features in the central zone. Also, the existence of the crater-like form can be registered and (ii) appearance of three damaged zones into periphery (Figs. 1C2; D2). On further periphery, hydro-dynamical features like resolidified droplets of materials can be distinguished.

The coating, prior to laser irradiation, was bright, silver-grey color and possesses mirror like surface with some dimly spots, Fig. 1A. In the course of irradiation process, the CrON surface has become darker. The degree of darkening increases with the number of pulses (N) up to two cumulated pulses. The change of sample color, in this case, can be attributed to chemical effects such as oxidation or to possible preferential sputtering. Additional increase of N, above 20, results in appearance of optically brighter parts on spot, which may originate from the coating amorphisation and material remelting.

The process of the TEA CO_2 laser interaction with the CrON coating was accompanied, from the beginning, by plasma appearance in front of the target. Spark-like plasma was typically created after first laser pulse. The degree of morphological changes of the CrON coatings, induced by laser radiation, can be considered by monitoring of damaged yield (DY) [4]. The results have shown that DY had changed rapidly, within first 100 successive laser pulses, and it remains almost constant, up to 400 pulses. In the latest case, one is to assume that interaction remained into bulk of the sample. By additional profilometer analysis of the damage shape and its depth, it was confirmed that significant material removal has started at 100 accumulated pulses. 3D- view of the CrON coating, after 400 pulses action, Fig. 3, shows that target damage has crater-like form. The ratio of the crater ($\sim 2.1 \times 10^{-4}\,\text{mm}^3$) missed material volume to the material volume, registered above the coating surface on periphery ($\sim 1.2 \times 10^{-4}\,\text{mm}^3$) was 1.75.

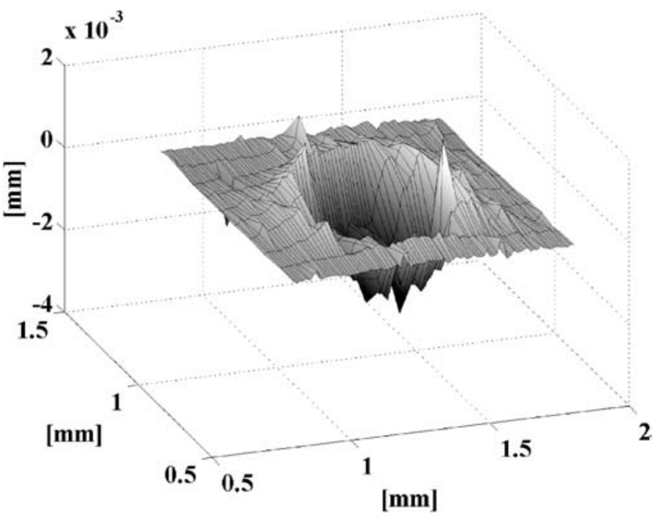

FIGURE 3 3D- view of the CrON coating after action of 400 cumulative laser pulses, based on profilometer analysis. 2D-view of coating is presented on Fig. 1.D1. (TEM_{00} mode; $F = 45.0\,\text{J/cm}^2$)

Materials redistribution is in correlation with the processes on the target, which may include, among others, vaporization, ablation, resolidification and oxidation. The action of 400 laser pulses on the coating leads to its ablation, but depth of modification (DM) is smaller in comparison to the CrON thickness, i.e., DM $< 3\,\mu\text{m}$.

4 Conclusion

The morphological changes on chromium oxynitride coating induced by the pulsed TEA CO_2 laser have been presented. The CrON coating was deposited by reactive sputtering technique on chromium, which was used as an intermediate layer between the coating and the AISI 304 steel substrate. Multi-pulse laser irradiation (up to 400 pulses) of the coating was performed in air. The laser energy density of $45.0\,\text{J/cm}^2$ has modified the coating. By profilometer analysis of the damage shape and its depth, it was confirmed that significant material removal has started at 100 accumulated pulses. The action of 400 laser pulses on the coating leads to its ablation, but depth of crater-like form is smaller in comparison to the CrON thickness. In case of used energy density, the interaction of laser radiation with CrON was always followed by creation of plasma in front of the coating.

Qualitatively the modifications of chromium oxynitride can be summarized as: central zone of interaction-non-uniform features with appearance of crater damage form; periphery zone of interaction-appearance of the three damaged areas. The change of the coating color suggests that chemical modification like coating oxidation was probable. On the further periphery the hydrodynamical effects like resolidified droplets can be detected.

ACKNOWLEDGEMENTS This research was financially supported by the Ministry of Science, Technologies and Development of the Republic Serbia (Proj. No. 1995 and 2018) and by Ministry of Sciences and Technology of the Republic of Slovenia.

REFERENCES

1 M. von Allmen: *Laser-Beam Interactions with Materials* (Springer-Verlag, Berlin 1987)
2 I.W. Boyd: *Laser Processing of thin Films and Microstructures* (Springer-Verlag, Berlin 1987)
3 D. Bäuerle: *Laser Processing and Chemistry* (Springer, Berlin 1996)
4 B. Gaković, M. Trtica, T. Nenadović, B. Obradović: Thin Solid Films **343–344**, 269 (1999)
5 J.C. Miller (Ed.): *Laser Ablation- Principles and Applications* (Springer-Verlag, 1994)
6 B. Navinšek, P. Panjan, I. Milošev: Surf. Coat. Technol. **116–119**, 476 (1999)
7 P. Panjan, B. Navinšek, A. Cvelbar, A. Zalar, J. Vlcek: Surf. Coat. Technol. **98**, 1497 (1998)
8 J. Bonse, H. Sturm, D. Schmidt, W. Kautek: Appl. Phys. A **71**, 657 (2000)
9 T.V. Kononenko, S.V. Garnov, S.M. Pimenov, V.I. Konov, V. Romano, B. Borsos, H.P. Weber: Appl. Phys. A **71**, 627 (2000)
10 M.S. Trtica, B.M. Gaković, T.M. Nenadović, M.M. Mitrović: Appl. Surf. Science **177**, 48 (2001)
11 J. Hermann, C. Boulmer-Leborgne, I.N. Mihailescu, B. Dubreuil: J. Appl. Phys. **73**, 1091 (1993)