Chemical analysis of thin-film’s colour generation during surface laser oxidation of TiN-coating

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Chemical analysis of thin-film’s colour generation during surface laser oxidation of TiN-coating

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Abstract. The phenomenon of metal surface colour change under laser exposure is quite unique. It’s most common explanation is based on the connection between the colour and the phase-composition of the generated films. However, the phase-composition analysis is a complicated and expensive process. As an alternative option we present a calculational method, based on a chemical thermodynamic approach. According to this method colour generation can be described by chemical reactions that lead to the formation of different compounds. And the formation of the most probable compound have the lowest level of the Gibbs Energy, which can be calculated. The proposed method was tested on the example of laser colouring of the surface of TiN-coating in the air environment. Calculations revealed that the most probable compound is titanium dioxide. Phase analysis based on X–ray diffraction proved the results of calculations.

1. Introduction
Titanium nitride thin-film coatings have chemical inertness, thermodynamic stability, high wear resistance and hardness. Such a wide variety of properties makes it possible to use it in the microelectronic industry, during manufacture of cardiovascular implants, as an absorbent layer in a selective solar absorber, the material of the coating for cutting tools or a wear-resistant and decorative coating [1-3].

At the same time formation of different colours on titanium, titanium nitride (figure 1, a), chromium (figure 1, b) and steel (figure 1, c) surfaces after laser treatment is a unique phenomenon which is a subject of the scientific interest [4].

Figure 1. Thin film’s colour generation on TiN-coating (a), chromium (b) and steel (c) surfaces.

Some authors [5] suggest that the colour of the surface depends not only on the interference in thin-film layers but also on the metal oxides’ intrinsic colours. These effects are determined by the thickness, transparency, and composition of thin films, formed during laser heating in the atmosphere.
Therefore it is important to determine the composition of the oxide films. At the same time, a compositional analysis is a complicated problem. That is why it is very important to develop various analytical and calculational methods for predicting results of the surface laser oxidation process. In the present study, the calculational method based on chemical thermodynamics was used for predicting the phase-chemical composition of colourful thin films formed by a laser oxidation of titanium nitride coating in the air.

2. Theoretical calculations
Thin film’s colour generation under laser exposure can be considered as a product of chemical reactions between metal surface and components of gas environment. The chemical thermodynamic method can be used for the identification of the possible and occurring interactions and their quantitative determination. According to the thermodynamic approach the best way to assess the probability of the occurrence of any interaction is to determine the Gibbs Energy \([\Delta G^0_T]\) of this reaction according to the formula:

\[
\Delta G^0_T = \Delta H^0_{298} - T \cdot \Delta S^0_{298} + \int_{298}^{T} C_p dT - T \cdot \int_{298}^{T} \frac{1}{T} \Delta C_p dT
\]

where \(\Delta H^0_T\) is the thermal effect of the process (enthalpy variation), \(\Delta S^0_T\) is the entropy variation of the system, \(C_p\) is the thermal capacity, and \(T\) is the working temperature.

Laser treatment is carried out in the atmosphere, the interaction between the titanium nitride and the most active air component – oxygen with formation different oxides (TiO, TiO\(_2\), Ti\(_2\)O\(_3\)) is most likely to happen. To determine if the oxide formation is thermodynamically permissible is possible by calculating the Gibbs Energy \(\Delta G^0_T\), using equation (1). Results of calculations of the Gibbs Energy \(\Delta G^0_T\) for possible chemical reactions between TiN and O\(_2\) are presented in Table 1.

| Reaction               | Product      | \(\Delta G^0_T\) (kJ/mol) |
|------------------------|--------------|---------------------------|
| 1 TiN+O\(_2\)=TiO+NO  | TiO          | -376                      | -355                      |
| 2 TiN+1/2O\(_2\)=TiO+1/2N\(_2\) | TiO        | -610                      | -466                      |
| 3 TiN+5/4O\(_2\)=1/2Ti\(_2\)O\(_3\)+NO | Ti\(_2\)O\(_3\) | -603                      | -574                      |
| 4 TiN+3/4O\(_2\)=1/2Ti\(_2\)O\(_3\)+1/2N\(_2\) | Ti\(_2\)O\(_3\) | -697                      | -652                      |
| 5 TiN+3/2O\(_2\)=TiO\(_2\)+NO\(_2\) | TiO\(_2\)        | -805                      | -763                      |
| 6 TiN+O\(_2\)=TiO\(_2\)+1/2N\(_2\) | TiO\(_2\)        | -815                      | -797                      |

Negative values of the Gibbs Energy \(\Delta G^0_T\) mean that all reactions can be completed in the temperature range 298-1000 K. However formation of TiO\(_2\) has the highest probability of occurrence as its Gibbs Energy is lower than that of TiO or Ti\(_2\)O\(_3\). According to calculations based on the thermodynamic approach, formation of TiO\(_2\) during laser oxidation of titanium nitride TiN is most likely to occur.

3. Experimental results
Laser treatment processes were studied on beryllium samples covered by TiN-coating. Samples were in the form of plates with a diameter 20 mm and a thickness of 4 mm. A thin film of titanium nitride coating was formed by cathodic arc deposition (PVD method). Nitrogen pressure was selected in the range from 0.1 to 0.2 Pa to create golden colour [7]. The samples were irradiated by exposure of a scanning beam of a fiber laser with a wavelength 1.06 \(\mu\)m and surface area with a diameter of 4 mm. The exposure was done under normal laboratory conditions in air. During experiments one mode was revealed that can change the colour of the titanium nitride coating from golden to blue by changing only the number of laser passes. A golden colour was obtained after the first pass, brown - after the
second laser scanning of exactly the same place, purple - after the third pass, and blue - after the forth pass. In the process, the pulse width $\tau$ was 4 ns, the average power $P_{ave}$, and the pulse repetition frequency $f$ were 5 W and 99 kHz, correspondingly. According to the theoretical calculations based on thermodynamic approach the most probable compound obtained after laser surface oxidation of titanium nitride coating is titanium dioxide.

XRD phase analysis was done using a Bruker D8 Discover diffractometer, and it revealed that generated colourful films consist of titanium oxide $\text{TiO}_2$ after the first, second, third and fourth laser passes. However, every next laser pass changed the sample colour as it’s shown in figure 2. Chemical elemental analysis was made using a scanning electron microscope Mira 3 Feg Sem, and it revealed the tendency of increasing level of oxygen in the titanium nitride coating with increasing number of laser passes: from 6% of oxygen for the first pass with the golden colour to 26% of oxygen for the last pass with the blue colour (figure 2).

![Figure 2](image_url)

**Figure 2.** Optical images of TiN-coating: (a) after the first laser pass, (b) after the second laser pass, (c) after the third laser pass, (d) after the forth laser pass.

Visual observation of laser oxidation process and analysis of optical images from figure 2 reveal that the image created by laser is formed by filling of lines. Every line consists of a set of point pulses. Each pulse is a cause of a sharp point heating that initiates a reaction between the titanium nitride coating and oxygen. As a result, there are points of titanium oxide inclusions in the titanium nitride coating.

Figure 3 shows SEM micrographs of TiN-coating before and after laser treatment, obtained using a scanning electron microscope Mira 3 Feg Sem.

![Figure 3](image_url)

**Figure 3.** SEM micrographs of TiN-coating: (a) before laser treatment, (b) after the first laser pass, (c) after the forth laser pass.

According to the images, presented in figure 3 (a), a thin film of titanium nitride coating has a homogeneous structure, repeating the substrate microrelief. Figure 3 (b) shows the SEM image of the TiN-coating obtained after the first laser pass. Figure 3 (c) describes the surface structure after the forth laser pass. It can be noted that laser treatment leads to the appearance of a network structure. Formation of such structure is most likely the result of phase transformation from titanium nitride to titanium dioxide. The network structure is caused by the replacement of nitrogen with oxygen in the coating composition.
4. Discussion
Thermodynamic calculations predicted the formation of titanium oxide TiO\(_2\) as the most probable compound after laser treatment of titanium nitride coating in the air. Phase analysis detected the appearance of titanium oxide TiO\(_2\) after the first, the second, the third and the fourth laser pass. Other oxides and compounds were not detected meaning that the experimentally obtained laser mode creates conditions for forming only TiO\(_2\). However, every next laser pass changes the sample colour. During experiments it was noticed that every next pass increases the size and the depth of the heated area where titanium nitride reacts with oxygen. Compositional analysis proved the tendency of increasing the level of oxygen in the TiN-coating with the increasing number of laser passes. It can be assumed that the color change is associated with the depth of oxidation process and the colour of the generated thin film is strongly depends upon its thickness and homogeneity. According to the publication [8], the color of titanium oxides varies with film thickness, since it is due to light interference phenomena taking place at the metal-oxide-air interfaces. So the thermodynamics approach can be used as a calculational method for prediction of formation of the most probable compound the amount of which can be increased by means of multipass laser processing.

Presented scientific results demonstrate that analysis of the phase and chemical transformations occurring at the surface of heated metals are generally governed by thermodynamics laws. Comparison of the calculated data with the experimental results demonstrates their good qualitative agreement. Furthermore, presented calculational method makes it possible to obtain the important detailed information about chemical reactions occurring under laser heating of a titanium nitride coating, niobium and chromium in a chemically active atmosphere.

5. Practical application
It should be noted that investigation of the phase and chemical modifications of the surface under laser exposure is important for many fields because of the variety of application areas of thin-film's color generation technology. It is successfully used as a technology image formation for providing functionality of optoelectronic read-out systems [7]. Medical implants are required to be marked for keeping them from falsification using the technology that keeps implants from surface damage during marking process [9-10]. Laser oxidation is applied as a technology intended for formation of dielectric layers [11] when manufacturing of microelectronic sensors. Laser coloration is also a very powerful tool for jewelry decoration.

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