Laser pulse structure dependent texture of FEL synthesized TiN_x coatings

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Abstract

Titanium was laser nitrided by means of free electron laser (FEL) irradiation in pure nitrogen atmosphere. The variation of macropulse frequency and duration of the FEL micropulse trains resulted in the formation of δ - TiN_x coatings with different thicknesses and different micro- and macroscopic morphologies. The coatings revealed characteristic values for hardness, roughness and crystallographic texture, which originate from the growth mechanism, the solid–liquid interface energy and the strain. Further investigations showed that the dendritic growth begins at the surface and the alignment of the dendrites is normal to the surface. A correlation of the texture with the time structure of the laser pulses was found. Combined numerical simulations of temperature evolution and nitrogen diffusion were performed and the results were compared with the experimental findings. The simulations can explain the experimental results to a great extent.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Titanium and its alloys play an important role as structural and functional materials in many fields. This originates from their superior corrosion resistance, high strength, low weight and low toxicity. The main disadvantage hindering even more usage is the low wear resistance of these materials. Concerning the improvement of wear resistance, nitriding of metals is an established technique [1]. Plasma and gas nitriding is frequently used and has been investigated in great detail [2]. A recent development is the use of laser radiation to process metals such as like Ti, Al or Fe in a reactive atmosphere [3]. The treatment with a free electron laser (FEL) is a possibility which has been employed very rarely so far [4]. First results of FEL nitrided titanium were reported in [5]. Here, additional investigations and simulations were carried out, in order to obtain more detailed information about the growth process,

solidification velocity and their effects on surface morphology and properties after this direct laser synthesis of TiN coatings.

The time-dependent description of the nitriding process is a difficult problem which could be solved by numerical computations. These simulations were compared with the experimental results of FEL laser nitrided titanium and they can explain the dendritic growth beginning at the surface leading to dendrites aligned perpendicular to the surface.

2. Experiments

2.1. Sample material

Pure α -Ti (purity >99.98%) was used for the treatments. The properties of titanium nitride, the binary Ti–N phase diagram and the solubility of nitrogen in α -titanium are well known. There are many publications [6] which describe the Ti–N

equilibrium phase diagram and the effects of the nitrogen concentrations on the melting temperature. The composition-dependent liquidus temperature, the maximum solubility of 23 at.% nitrogen in α -Ti [7] without any formation of a stable phase and the variation of the lattice parameter as a function of nitrogen content in TiN_x as given in equation (1) [8] are important facts for the presented results. This equation corresponds to Vegards law, [9, 10]:

$$a = 4.1925 \text{ \AA} + x \cdot 0.000467 \text{ \AA}. \quad (1)$$

The titanium was cut into pieces of $15 \times 15 \text{ mm}^2$ size and 1 mm thickness. The samples were used in the as-cast and as-cut state without any further treatment. The virgin surface roughness of the samples was in the order of $R_a = 100 \text{ nm}$.

2.2. FEL treatments

The FEL irradiation was carried out at the infrared FEL of the Thomas Jefferson National Laboratory in Newport News (Virginia, USA). The used FEL radiation had a wavelength of $3.1 \text{ }\mu\text{m}$. The FEL radiation consisted of micropulses with 0.5 ps pulse duration and 37.4 MHz repetition rate at a mean micropulse energy of about $20 \text{ }\mu\text{J}$. Macropulses with durations of 250 to $1000 \text{ }\mu\text{s}$ at repetition rates f_{ma} 10 to 60 Hz were formed out of these micropulses, i.e. these macropulses consist of a train of micropulses. Thus, the macropulse energy ranged from 0.04 to 0.75 J. The raw Gaussian-like FEL beam was focused by means of a CaF₂ lens to a spot size of $D_b = 0.440 \text{ mm}$ on the sample surface. Therefore, a macropulse fluence of several hundred J/cm^2 could be imposed onto the titanium samples' surfaces.

For the laser nitriding, the samples were placed in a chamber, which was first evacuated and then filled with nitrogen gas (purity 99.999%) to a pressure of 10^5 Pa . The beam reached the sample surface through a fused silica window. In order to treat the whole surface of the samples, the chamber was mounted onto a computer-controlled x - y table. A relative velocity of $v = 0.5 \text{ mm s}^{-1}$ in the x -direction was used. The y -direction movement was represented by a lateral shift δ of 100 or $200 \text{ }\mu\text{m}$ after each x -scan. The whole surface of the sample was irradiated by this kind of movement (meandered scan) and the irradiation of the surface can be described by means of the dimensionless overlap parameter,

$$\sigma = \frac{D_b^2 \cdot f_{\text{ma}}}{v \cdot \delta}, \quad (2)$$

which indicates how often every point of the surface is hit by a macropulse. Thus, σ allows a comparison between different experimental setups and the achieved coating properties. A set of four samples is presented here, which were produced with the parameters given in table 1.

Due to the interactions of the laser beam with the titanium surface, a plasma is formed above the titanium surface and nitrogen diffuses into the titanium as a function of the treatment parameters involved. This correlation was investigated in greater detail.

Table 1. Macropulse duration τ_{ma} , macropulse repetition rate f_{ma} , lateral shift δ (in y -direction) and overlap σ used for the FEL treatments. The velocity in x -direction is always 0.5 mm s^{-1} .

Sample	τ_{ma} (μs)	f_{ma} (Hz)	δ (μm)	σ
1	250	60	100	232
2	750	30	100	116
3	1000	30	100	116
4	1000	10	200	19

2.3. Sample analysis

After the FEL laser treatments, the samples were examined by means of a scanning electron microscope (SEM). Cross section micrographs were prepared after mechanical and ion polishing. For the surface pictures, the electron detector was rotated by 30° relative to the samples. All cross section micrographs were taken with backscattered electrons, i.e. there is a good contrast between the nitrided areas and the pure titanium regions. Darker areas in the micrographs have a higher nitrogen content.

Additionally, the SEM was equipped with energy dispersive x-ray (EDX) analysis, which has been utilized to determine the nitrogen content at several points of each sample. Due to the superposition of the titanium L line and the nitrogen K line in the spectra and the deficient energy resolution of the detector (30 eV are required) [11], only qualitative statements were possible. However, different regions such as the melting, diffusion and heat affected zone could be compared.

Complementary hardness, surface profile and x-ray diffraction (XRD) measurements were carried out. In order to obtain information about the mechanical properties, microhardness depth profiles were measured with a nanoindenter (Fischerscope HV100). It operates with a Vickers diamond tip and a maximum force of 1 N [3]. Subsequently, a roughness measurement with a surface profiler (Dektak) was performed to check the surface roughness and the light sample bending as a result of thermal/mechanical stresses.

The microstructure of the layers was investigated with XRD in Bragg-Brentano and grazing incidence geometry (GIXRD), rocking curve scans (200-peak) and texture measurements utilizing a Bruker AXS diffractometer equipped with a Cu-K α tube. With these measurements, the relations between the crystallographic structure and the mechanical properties could be determined.

3. Numerical simulations

A numerical simulation of the nitriding process was established, in order to understand the laser nitriding process details not accessible experimentally. Especially, the missing possibilities for time resolved measurements of plasma and melt bath dynamics were attempted to be accessed numerically. The starting point is the solution of the heat diffusion equation for laser heating:

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) + \alpha e^{-\alpha z} (1 - R) I(\vec{r}, t) - \vec{V} \rho c_p \nabla T. \quad (3)$$

The recession velocity $\vec{V}$ [12] has been neglected, i.e. the last term in equation (3) vanishes. In contrast, phase transitions

Figure 1. Temperature-dependent heat capacity c_p (data taken from [13]) and thermal conductivity κ (data taken from [14]) used in the simulations. The area of the rectangles at the melting and evaporation points represent schematically the latent heat of fusion and evaporation (the box height not to scale here).

and stock removal, which starts when the evaporation temperature is reached, are considered in the calculations. A stationary description was used for the numerical solution, because the sample movement v relative to the laser beam was much slower than the pulse structure of the FEL laser beam. The specific heat c_p and thermal conductivity κ have been assumed to be temperature dependent with values shown in figure 1. The numerical values have been taken from [13, 14]. In order to consider the latent heat of melting L_m and evaporation L_{ev} , the specific heat was raised for a short temperature range (5 K) around the transition temperature, so that the area of these rectangles corresponds to the relevant latent heats, as indicated in figure 1.

This has to be coupled with the partial differential equation of temperature-dependent diffusion. Classical diffusion processes are described by Fick's second law, which is also valid for the laser nitriding process and was used to calculate the nitrogen depth profile:

$$\frac{\partial c(z, t)}{\partial t} = \frac{\partial}{\partial z} \left(D(T) \frac{\partial c(z, t)}{\partial z} \right). \quad (4)$$

The used boundary conditions were $c(0) = 0.5$, $c(\infty) = 0$, according to previous measurements of the nitrogen concentration [5]. The temperature dependence of the nitrogen

Table 2. Physical properties of Ti and TiN used in the simulations.

Parameter	Symbol	Value	Reference
Ti melting temperature	T_m	1941 K	[20]
Ti boiling temperature	T_b	3560 K	[20]
Ti latent heat of fusion	L_m	18 kJ mol ⁻¹	[21]
Ti latent heat of evaporation	L_{ev}	420 kJ mol ⁻¹	[21]
Ti reflectivity	R	≈ 0.73	[22]
(at $\lambda = 3.13 \mu\text{m}$)			
Ti absorption coefficient	α	$52 \times 10^6 \text{ m}^{-1}$	[20]
(at $\lambda = 3.13 \mu\text{m}$)			
Ti molar mass	M	47.89 g mol ⁻¹	[20]
Ti density	ρ_{Ti}	4.52 g cm ⁻³	[20]
TiN latent heat of fusion	L_{TiN}	67 kJ mole ⁻¹	[23]
TiN molar mass	M_{TiN}	61.91 g mol ⁻¹	[23]
TiN melting temperature	$T_m(\text{TiN})$	3220 K	[21]
TiN density	ρ_{TiN}	5.33 g cm ⁻³	[24]

diffusion coefficient $D(T)$ was recalculated using data taken from [15], which is based on a previous study by Wood and Paasche [16] on heating of titanium. They are somewhat different from [17, 18] used for gas nitriding of titanium. Nevertheless, the temperature and time scales in the present case are much different. Thus $D(T)$ represents a typical Arrhenius behaviour:

$$D(T) = D_0 \cdot \exp \left(-\frac{Q}{RT} \right), \quad (5)$$

with $D_0 = 0.12 \text{ cm}^2 \text{ s}^{-1}$ and $Q = 189.8 \text{ kJ mol}^{-1}$. Furthermore, the mass density ρ , the thermal conductivity κ and the specific heat c_p are functions of the nitrogen concentration c . The density is simplified by

$$\rho(c) = \begin{cases} \rho_{\text{Ti}} + (\rho_{\text{TiN}} - \rho_{\text{Ti}}) \cdot \frac{c}{c_\alpha}, & \text{for } c < c_\alpha, \\ \rho_{\text{TiN}}, & \text{for } c \geq c_\alpha, \end{cases} \quad (6)$$

where $c_\alpha = 0.23$ is the solubility limit of nitrogen in α -Ti [19].

A similar lever rule was applied for estimating the thermal properties for a nitrogen concentration dependent mixture of Ti and TiN. In TiN, the nitrogen concentration lies between the lower concentration boundary for TiN ($c_{\min} = 0.33$) and the maximum observed nitrogen concentration ($c_{\max} = 0.72$) [19].

The temporal shape of the laser intensity has been taken as constant over the pulse duration and the lateral distribution of the FEL laser beam was assumed to be Gaussian with a variance of $\sigma_b = D_b/2.35$, such that the heat flux into the surface was expressed by

$$q(z=0) = (1-R) \cdot I_0 \cdot \exp \left(-\frac{(x^2 + y^2)}{2\sigma_b^2} \right). \quad (7)$$

The intensity of the laser is $I_0 = 3.37 \times 10^9 \text{ W m}^{-2}$. The optical absorption coefficient α and the reflectivity R were assumed to be temperature independent (i.e. constant), because no other data were available.

Thus, we end up with a mathematical model, where all quantities are formally known. The model consists of a coupled system of nonlinear time-dependent partial differential equations. The equations are discretized in space using a finite element model (FEM). For the discretization in time we used an implicit scheme. For all the numerical simulations we used the multiphysics software COMSOL 3.2TM [25]. Table 2 summarizes all the numerical values used for the simulations.

Figure 2. Simulated melting depths for different pulse durations: (a) 0.25 ms, (b) 0.75 ms, (c) 1 ms and surface temperatures (d). Additionally, the calculated N diffusion depth profiles and the solidification velocities are shown. (The diffusion depth is defined as the depth where the nitrogen concentration has dropped to $1/e^2$ of the surface concentration. ($2\tau_p$) gives the situation after 2 subsequent laser pulses.)

As a result of the numerical simulations, the temperature reaches the evaporation point after 730–750 μ s, as shown in figure 2. An estimation of the stock removal can be made by the use of the Clausius–Clapeyron equation:

$$p(T) = p_0 \cdot \exp \left[\frac{L_{ev}}{N_A k_B} \left(\frac{1}{T_b} - \frac{1}{T} \right) \right]. \quad (8)$$

All parameters are known and an evaporation thickness of $\Delta h \approx 6\text{--}8\text{ }\mu\text{m}$ for a pulse duration of 1 ms is estimated. In addition, it is possible to calculate the liquid–vapour interface velocity:

$$v_{ev}(T) = \frac{p(T)}{\rho \sqrt{2\pi N_A k_B T/M}}. \quad (9)$$

The duration of evaporation t_{ev} has been taken from the simulations. It is the time where the alpha titanium has a temperature above its evaporation temperature (with a value of nearly 300 μ s). The ambient pressure p_0 is supposed to be 10^5 Pa.

$$\Delta h = \int_0^\infty v(t) dt \approx v_{ev}(T_{ev}) \cdot t_{ev}. \quad (10)$$

Additionally, the very important independence of stock removal from the overlap parameter needs to be considered, because only during the first time of heating a surface element will be evaporated. After the first laser irradiation, we develop

a coating of TiN, which has a much higher evaporation temperature. The stock removal has been included in the simulations, as shown in figure 2(c). The line (corr. N diffusion) indicates this stock removal. Such evaporation processes always induce a high vapour pressure, which can affect the liquid surface. The problem of this influence still needs to be solved, possibly by means of investigations of stress and strain, which have to be studied as well.

The main information was obtained from the solidification front. Following the simulations, a solidification velocity of about 2 cm s^{-1} was achieved, astonishingly in the top–down direction. Moreover, the temperature gradient is gained, which deduced the solidification mechanism.

The solidification is indeed dendritic, as will be shown later in the cross sections. In a further step, a quantitative description of the dendritic growth during FEL laser nitriding will be tried.

4. Experimental results

4.1. Surface

Figure 3 shows the surface of the nitrided samples. Figure 3(a) depicts a rough surface caused by solidified melting droplets. In addition, there are a lot of cracks, which indicate that the surface is very brittle with a high amount of intrinsic stress. For technical applications such surfaces are unsuitable.

Figure 3. Surface morphology of the samples: (a) sample 1 (250 μ s), (b) sample 2 (750 μ s), (c) sample 3 (1000 μ s) and (d) sample 4 (1000 μ s). Melting droplets and cracks are observed (scale valid for all).

Figure 4. Surface profiles showing the dependence of roughness, bending, rifts, droplets and cracks on the laser pulse time structure.

Fewer droplets can be observed for the second sample. This is a result of prolonged pulse durations and lower pulse frequencies. However, there are still rifts, which make the coatings fragile.

Further, the pulse duration was increased to 1000 μ s which avoided melting droplets because the evaporation temperature was exceeded after 750 μ s. During the last quarter of the pulse duration, the topmost layer evaporated and the surface assumed the properties of vaporized coatings, though the network of rifts still existed. With respect to the simulation, it can be postulated that the network emerged before the evaporation started. Large gaps divide the layer into small islands, leading to bad mechanical properties.

Finally the pulse frequency was further reduced to 10 Hz and the line shift was raised and the implemented energy reduced to 25%. As a result of this action a coating without large rifts and droplets could be obtained. This fourth nitrided sample reached an acceptable quality, but further investigation and variation of the parameters are necessary to optimize such surfaces.

Figure 4 shows the surface profiles and their average arithmetic roughness R_a . As seen, the R_a of sample 1 is three times that of sample 4. Maybe, this is based on avoiding melting droplets and cracks when reaching the evaporation temperature and getting an optimized temperature distribution. In order to achieve this aim, one has to find the optimal relation between overlap, pulse shape and duration of vaporization. In addition, a light convex bending is observed for all samples, probably as a result of thermal stress. This stress cannot be avoided, but it could be minimized by an optimized power/timing/velocity relation. These assumptions are in good agreement with the results of the numerical simulations, where the evaporation temperature is significantly exceeded only for

Figure 5. Cross sections of laser nitrided titanium. The lines show the simulated diffusion depth for samples 1 (250 μ s), 2 (750 μ s) and 3/4 (1000 μ s). The dendritic growth, the results of convection dynamics and the anisotropic nitrogen distribution are depicted. Scale is valid for all.

sample 4, which leads to the vanishing of melting droplets. This should be a general condition for smooth surfaces. From the GIXRD measurements a nitrogen concentration close to 50 at.% could be detected in all cases ($c_N = 0.50(4)$). Thus, the TiN phase is always close to stoichiometry (at least on the surface).

4.2. Cross sections and heat affected zone

Cross section SEM micrographs are shown in figure 5, where the melting depth can be determined to range from 20 up to 80 μ m for different samples. All the samples could be divided into nitrided, melted and heated zones, whose thicknesses are determined by the nitriding parameters. Bad coating properties are shown for sample 1 here too. Melting droplets and cracks dominate the structure. The crystallization is not oriented, and only some grains are visible, their number depending on the diffusion depth. Furthermore, the thickness is in the order of magnitude of the roughness. Therefore, the layer is not homogeneous.

Dendrites of TiN are shown in the other samples. The growth direction is mostly perpendicular to the surface. Between the dendrites there are areas with a lower nitrogen content. Cracks could only be found in the TiN_x areas. The most powerful irradiated sample is sample 3. Large cracks can be observed, as a result of the high inrushing energy and the subsequently produced stresses. As shown later, the XRD shows a (2 0 0) texture but fewer dendrites are available. This is due to remelting of the coating many times and it can be taken as an indication of an overdosed energy entry, which induces stress and convection.

Figure 6. Cross sections of the laser nitrided titanium. The marks indicate the locations for the EDX measurements, whose results are shown in table 3.

Table 3. Nitrogen contents as obtained by EDX in atomic per cent (at.%). The measuring points are indicated in figure 6.

Sample	EDX1	EDX2	EDX3	EDX4
1	23.75	7.61	6.89	5.30
2	26.84	16.09	7.26	6.77
3	22.95	26.27	6.09	5.41
4	28.17	10.36	8.11	5.57

Finally, sample 4 reached acceptable properties. Occasional cracks could be observed, but there were no melting droplets and a small roughness. The growth direction is perpendicular again and exclusively dendritic. Between the grain kernels and their shells α -martensite titanium still remained. All this points towards a nitriding setup, where overlap, laser energy and solidification produce the best coating.

4.3. EDX-measurements

In addition to the cross sections, EDX was employed at several points in figure 6 in order to determine the nitrogen content as well. On account of the overlaying spectral lines (titanium L line and nitrogen K line) the results give only a qualitative overview. Anyway, the TiN phase and the nitrogen content below the nitrided layer can be measured. Below the nitride layer and above the melting zone depth, all measurements result in a nitrogen content of about 5 at.%. There is no nitrogen in the titanium below the melting depth. At the melting depth, a small content of nitrogen was detected. Within the nitride layer, there are areas with dense δ - TiN_x crystallites interconnected with α - Ti(N) regions with a lower nitrogen content. This results from the solubility of nitrogen in α -Ti. A nitrogen concentration of 23 at.% could be reached without forming TiN .

Figure 7. Hardness depth profiles as measured by the nanoindenter.

4.4. Physical properties

Primarily, hardness is a material property that is interesting for technical applications. It is correlated with wear resistance and other tribological properties.

Figure 7 presents the hardness depth profiles of the samples and it becomes obvious that only sample 4 reached the expected hardness of TiN . The others reflect the bad surface properties already mentioned before. During the nanoindentation measurements melting droplets and rifts were hit, and further cracks may have occurred during the mechanical loading, resulting in the observed inhomogeneous depth profiles.

4.5. XRD analysis

Figure 8 shows the θ - 2θ spectra of the laser nitrided samples. TiN is cubic (space group F_{m3m} (225)) and has a lattice

Figure 8. XRD patterns measured in Bragg–Brentano geometry for samples 1 (250 μ s), 2 (750 μ s) and 3/4 (1000 μ s). TiN peaks are indexed, all other peaks belong to α -Ti.

Figure 9. Rocking curves of the (200) peak, a clear hint to strong textures as a result of dendritic growth. (1 (250 μ s), 2 (750 μ s) and 3/4 (1000 μ s)).

constant of $a = 4.241 \text{ \AA}$ [26]. The virgin titanium is hexagonal (space group $P6_3/mmc$ (194)) and has lattice constants of $a = 2.950 \text{ \AA}$ and $c = 4.682 \text{ \AA}$ [26]. The (200) reflection starts to dominate with more extended pulse durations. Its growth and dominance indicate a (200) texture of δ -TiN_x, which could be proven by rocking curve scans shown in figure 9 and the pole figures displayed in figure 10.

A texture parameter η is defined as the ratio of (111) to (200) peak intensities, i.e. $\eta = I(111)/I(200)$. η decreases with the sample number, as the (200) texture increases. $\eta = 0$ gives a perfect (200) texture, whereas $\eta = 0.72$ is obtained for a perfect polycrystal without any texture.

By means of peak position and peak broadening it is possible to extract the strain and grain size in the sample [27, 28]. The relation between peak width B_{hkl} (Cauchy profiles are used here), peak position θ_{hkl} , and strain ϵ is given by equation (11) [28]:

$$B_{hkl} \cos(\theta_{hkl}) = \frac{k\lambda}{L} + \epsilon_{hkl} \sin(\theta_{hkl}). \quad (11)$$

Figure 11 shows the extracted strain as a function of the texture parameter η and an increasing strain is observed for stronger (200) textures.

Figure 10. Pole figures of the (200) reflection for samples 1 and 4.

Figure 11. Calculated strain as a function of texture parameter η for the samples.

A study of this growth has been executed by several authors [29–31]. In all works, the total energy was taken as a sum of different terms resulting from Gibb's energy, strain and other influences. For high stress levels, the surface energy is minimized normal to the (111) direction. In the case of TiN this is the (200) direction. A precise treatment is found in [30]. A quantitative description of dendritic growth during FEL nitriding is in progress.

5. Conclusions

It was shown that laser nitrided titanium reached different coating qualities and properties as a result of the variation of the treatment parameters. Coating thicknesses of about 5 to 70 μ m with varying nitrogen content and different growth morphologies were observed. The surface characteristics are determined by pulse duration and the overlap parameter. A hardness of about 8 GPa could be reached for the best sample, representing a surface without cracks and melting droplets. This result is dependent on heat transfer, solidification and strain. In order to obtain surfaces with a small roughness, it seems necessary to exceed the evaporation temperature.

Numerical simulations of the nitriding process were successfully applied to achieve time resolved information for a deeper understanding of the growth processes. As a result of solidification velocity and temperature gradients, dendritic growth was observed. It follows from solid–liquid interface properties such as enthalpy and stress, affected by the nitriding parameters. The texture development could be related to the

treatment parameters with the help of the simulations. These simulations might help to reach TiN coatings with the best possible properties. As an outlook, the convection in the melt has to be added to the simulations, which probably mingles the melting zone and changes the nitrogen depth profiles.

Altogether it seems possible to produce coatings by FEL nitriding, but the quality still has to be improved.

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