

The Influence of the Coating Thickness on the Phase and Element Composition of a 'Ti Coating/Steel' System Surface Layer Treated by a Compression Plasma Flow

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The phase and element composition, microhardness of a 'Ti/steel' system mixed under the action of compression plasma flows have been investigated in this work. Non-Rutherford backscattering, X-ray diffraction, scanning electron microscopy and Vickers microhardness measurements were used for samples characterization. The findings showed that the change of the coating thickness in the range of 0.5–5 μm resulted in the Ti concentration change in the mixed layer from 4 to 30 at.-%. The increase of the titanium content was accompanied by the formation of a supersaturated $\alpha\text{-Fe(Ti)}$ solid solution, Fe_2Ti and TiN . The phase composition changes and quenching effect led to the surface layer microhardness increase.

Introduction

Mixing of a 'coating/substrate' system by ion, electron, plasma and laser beams is one of the possible alloying techniques.^[1–12] The change of treatment parameters and a coating material allows to form a variety of alloys in the surface layer of substrate materials with enhanced corrosion resistance,^[6,8] hardness,^[2,5,11] friction coefficient and

wear resistance.^[2,7,9] This technique is also suitable for semiconductors properties modification.^[3,4]

Compression plasma flows (CPF) can also be effectively used for mixing of a 'coating/substrate' system, thus leading to alloying of a substrate with atoms of coatings and a plasma forming gas. CPF generated by quasi-stationary plasma accelerators are characterized by the presence of a compression area in the middle of a plasma flow appeared due to the interaction of a longitudinal component of the discharge current 'swept away' from the discharge device with the intrinsic azimuth magnetic field.^[13] CPF possess a comparatively long discharge time ($\sim 100 \mu\text{s}$), a high temperature (1–3 eV) and a high velocity ($4\text{--}7 \times 10^6 \text{ cm} \cdot \text{s}^{-1}$) of plasma particles. These main CPF parameters lead to the melting of surface layer and liquid phase mixing resulting in the formation of a mixed layer with the thickness of $\sim 10\text{--}15 \mu\text{m}$ after the 'coating/steel' system treatment.^[14] The mixed layer formation can be described in the following way.^[14,15] At the first stage a coating consisting of one or a few elements to be alloyed is deposited on the surface of the material. At the second stage CPF treatment of the formed system is carried out. CPF impact with the surface is accompanied by ablation of some

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part of the coating, thus diminishing the volume of the alloying element appearing in the mixed layer, and by melting of the coating left and of some part of the substrate material. The temperature of the melted layer can reach $3-4 \times 10^3$ K.^[16] The period of the melt layer existence is of the order of discharge time $\sim 10^2$ μ s.^[16] A high concentration and temperature gradients in the melted layer due to the dependence of the surface tension on the concentration and temperature lead to concentration-capillar and thermo-capillar (Marangoni) convection.^[17,18] Convection whirls which appeared in the liquid phase lead to the mixing of the coating and substrate elements in the melting layer. Subsequent crystallization of the melted layer at a high cooling rate ($\sim 10^7$ K s⁻¹) results in the formation of the mixed layer with the same thickness containing elements of the coating and the substrate. Besides that diffusion of atoms from residual atmosphere (e.g. nitrogen if it is used as a plasma forming gas) can take place in a thin surface layer (~ 1 μ m).^[16] The previous investigations on CPF treatment of Zr/AISI M2 steel system showed that one pulse of treatment did not provide a homogeneous elements distribution in the mixed layer due to shortage of convection time.^[15] That is why the increase of the pulses number should result in a more uniform distribution of elements.

The element composition in the mixed layer can be controlled by changing treatment parameters: the energy transferred to a sample per pulse and the number of pulses.^[14,15] After one pulse of treatment the average concentration of the alloying element \bar{c} can be roughly estimated (without taking into account ablation and diffusion from the mixed layer) as $\bar{c} = t_{\text{coat}}/t_{\text{mix}}$, where t_{coat} is the thickness of the preliminary deposited coating and t_{mix} is the thickness of the mixed layer. The previous experiments (coating thickness $\sim 1-2$ μ m) showed that the concentration of the alloying element did not exceed ~ 15 at.-%.^[14,15] The growth of the energy transferred to a sample per pulse due to the increase of coating material ablation and melted layer thickness led to the decrease of the alloying element concentration.^[15,16] Ablation is also responsible for the alloying element decrease in case the number of pulses grows.

Another way of the alloying element concentration change is a variation of the coating thickness. This approach allows to increase the concentration of an alloying element, thus expanding the range of synthesized alloys (assuming that the thickness of a coating is less than that of the mixed layer). Thus, the influence of the CPF treatment on the phase and element composition as well as microhardness of a 'Ti coating/carbon steel' system with different coating thickness were investigated in this work.

Experimental Part

The samples used were made of a carbon steel (0.2% C, 0.2% Si, 0.5% Mn, in wt.-%). The titanium coating was formed using cathodic arc

vapour deposition with the following process parameters: the arc current of 100 A, the bias voltage of -120 V, the deposition time 2, 5, 10, 20 min (the corresponding coating thickness 0.5, 1.2, 2.5, 5.0 μ m).

CPF were obtained using a gas-discharge magneto-plasma compressor (MPC) of compact geometry powered with the capacitive storage of 1200 mF, operating at the initial voltage of 4 kV. The discharge device and principles of CPF generation were described in detail earlier.^[13] Nitrogen was used in the MPC as a plasma forming gas. The pressure of residual gases in the vacuum chamber before nitrogen input was 10^{-1} Pa. The pressure of the plasma forming gas was 400 Pa during the discharge. The discharge duration in the MPC amounted to ~ 100 μ s. The treatment of the formed Ti/steel system was carried out by three pulses of CPF to provide homogeneity of the mixed layer. The time interval between pulses was 30–40 s. The energy density absorbed by the surface layer was ~ 13 J cm⁻² per pulse.

The element composition was investigated by means of the non-Rutherford backscattering analysis (nrBS) of He ions with the energy of 6 MeV. A high energy of helium ions allowed to increase the yield of ions scattered on light impurities due to resonance. Non-Rutherford cross-sections were used for the calculation. The phase composition of the samples was investigated by the X-ray diffraction analysis (XRD) in Bragg–Brentano geometry and Cu K α radiation using a DRON 4–13 diffractometer. The cross-section morphology and element composition were analysed by means of scanning electron microscopy (SEM) using a LEO1455VP device equipped with an energy-dispersive X-ray Röntec detector. Before SEM investigations the samples cross-section were etched in 3% HNO₃ + 97% C₂H₅OH solution. The microhardness of the samples was tested by means of a PMT-3 microhardmeter with a Vickers indenter under the load ranging from 1 to 2 N. The minimum load of 1 N on the indenter was chosen to diminish inaccuracy of measurements because the samples surface had developed roughness after treatment.

Results and Discussion

The element composition analysis showed that the growth of the coating thickness led to the increase of the Ti concentration in the bulk of the mixed layer (Figure 1). The corresponding concentration for the coating thickness of 0.5, 1.2, 2.5 and 5.0 μ m amounted to 4.0 ± 0.3 , 8.0 ± 0.6 , 15.0 ± 0.8 and 30 ± 1 at.-%, respectively. These data are in good agreement with the results of the energy-dispersive X-ray microanalysis (3 ± 1 , 11 ± 2 , 14 ± 2 and 31 ± 3 at.-%, respectively). Thus, one can find almost a linear dependence of the Ti concentration on the Ti coating thickness in the used range of the experimental parameters. NRBS spectra also contained carbon, nitrogen and oxygen peaks that appeared due to diffusion of vacuum chamber residual atmosphere elements into samples during treatment (Figure 1). At the same time the distribution type of nitrogen and oxygen in the samples is not diffusion-like. The thickness of the surface layer containing nitrogen and oxygen is about 50–70 nm. The nitrogen concentration in this layer is about 20–25 at.-% and is almost constant for all

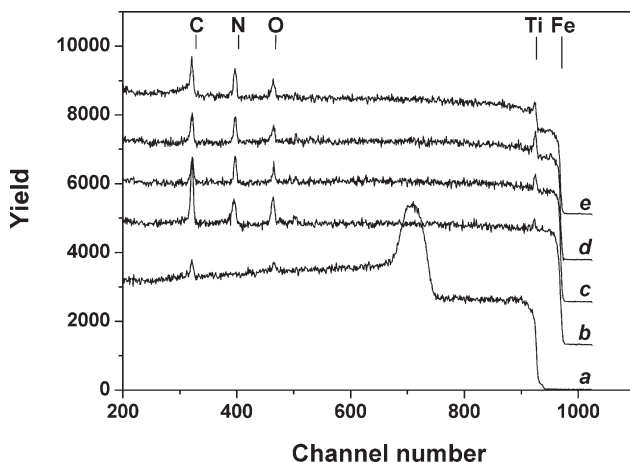


Figure 1. The nRBS spectra of the Ti/steel system sample with the coating thickness of 2.5 μm before treatment (a) and samples with the coating thickness of 0.5 μm (b), 1.2 μm (c), 2.5 μm (d) and 5.0 μm (e) treated by CPF.

treated samples. The distribution of titanium is not uniform in the surface layer. The Ti distribution has a surface segregation peak (just in the layer containing light impurities). The underlying layer (up to $\sim 0.4 \mu\text{m}$) lacks titanium. Possible reasons for such alloying element behaviour were discussed earlier.^[15]

The change of the alloying element concentration in the mixed layer influences its phase composition (Figure 2). The XRD analysis showed a shift of $\alpha\text{-Fe}$ diffraction lines to smaller angles with the growth of the titanium concentration. A possible reason for this effect is the formation of a supersaturated $\alpha\text{-Fe}(\text{Ti})$ solid solution where Ti atoms substitute Fe atoms in the bcc lattice. Ti solubility in $\alpha\text{-Fe}$ does not exceed 2.9 at.-% even at 500 °C in equilibrium conditions.^[19] In our case $\alpha\text{-Fe}(\text{Ti})$ is the only phase that can be seen by XRD if the Ti concentration is up to 8 at.-% except of TiO_2 phase (from the thin surface layer) that can be seen at low angles for all treated samples. A further increase of the Ti concentration up to 15 at.-% led to the formation of TiN with a (200) preferred orientation. The element composition analysis showed that the nitrogen concentration in the surface layer was almost constant as well as the thickness of the nitrogen containing layer for all samples (Figure 1). Thus, the appearance of TiN diffraction peaks is connected with the growth of the Ti concentration. The increase of the Ti concentration up to 30 at.-% led to the growth of the TiN volume fraction and precipitation of Fe_2Ti phase.

Earlier it was found that the type of nitrogen distribution in a steel treated by CPF was diffusion-like.^[16] In our case the presence of titanium possessing very low nitride and oxide formation enthalpy changes a type of nitrogen (as well as other light elements) distribution. The titanium oxide and nitride thin surface layer formation prevents diffusion of carbon, nitrogen and oxygen from the residual

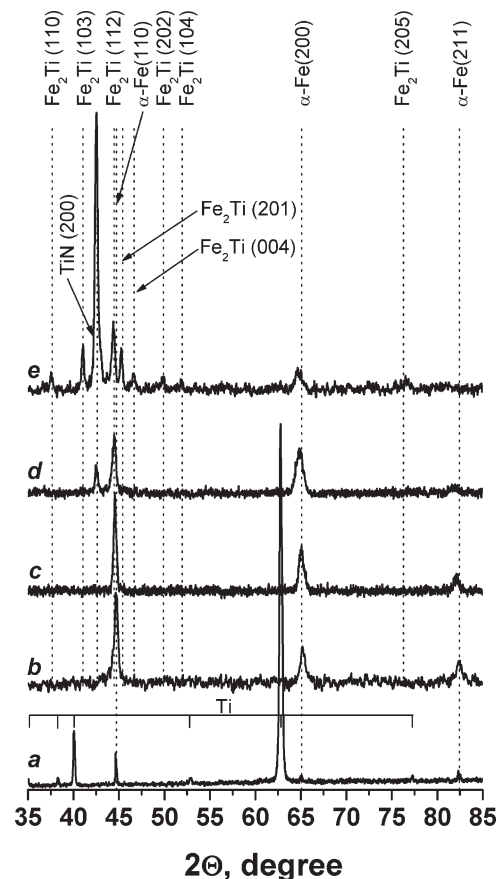


Figure 2. The XRD patterns of the Ti/steel system sample with the coating thickness of 2.5 μm before treatment (a) and samples with the coating thickness of 0.5 μm (b), 1.2 μm (c), 2.5 μm (d) and 5.0 μm (e) treated by CPF.

atmosphere of the vacuum chamber into the bulk of the sample. This effect can explain non-diffusion distribution of light impurities and can also be a reason for titanium surface segregation.^[15]

The analysis of the cross-section morphology and elements distribution along the depth showed almost uniform distribution of titanium in the mixed layer (Figure 3). For the samples with the coating thickness up to 2.5 μm the thickness of the mixed layer is almost constant $\sim 10 \mu\text{m}$. The growth of the coating thickness up to 5 μm results in the decrease of the mixed layer thickness (Figure 3f). This is the effect of smaller thermal conductivity of titanium [the coefficient of thermal conductivity at 1 000 K is 21 W/(m · K)]^[20] in comparison with that of the steel [33 W/(m · K)].^[20] Smaller thermal conductivity of the surface layer results in the decrease of the melted layer thickness and hence, the mixed layer thickness.

Two main layers can be found in the modified zone (Figure 3c): a mixed layer—layer A and a heat affected layer—layer B. The heat affected layer with the thickness of $\sim 20 \mu\text{m}$ can be seen in the figure due to a changed structure

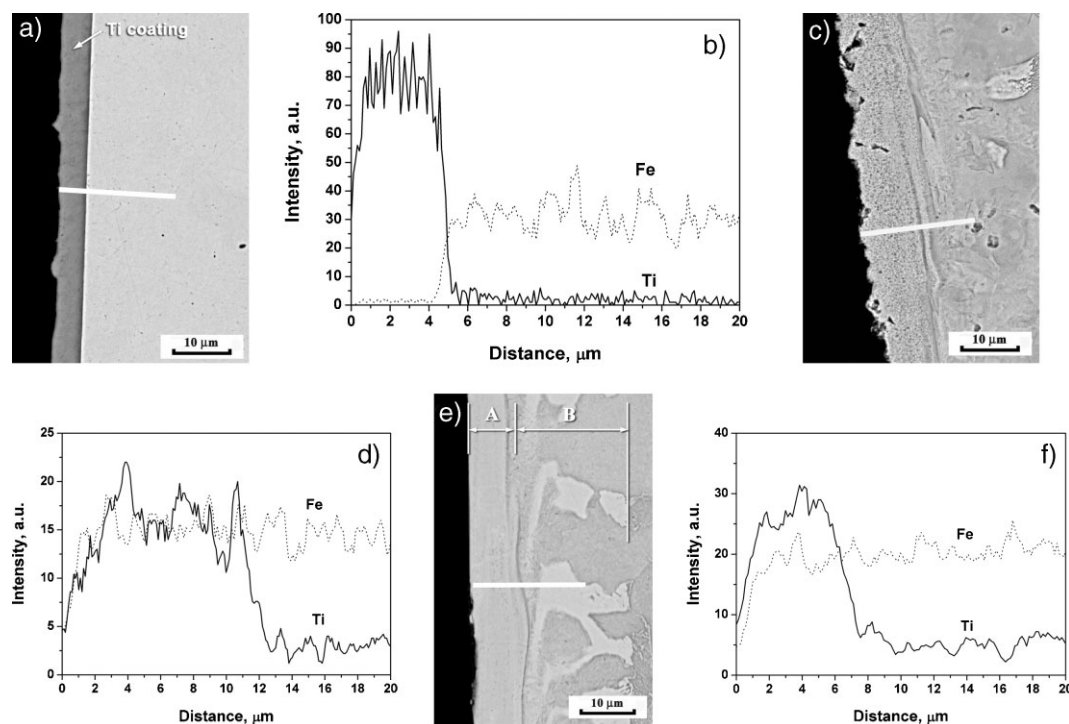


Figure 3. Cross-section morphology (a, c, e) and distribution of elements along the corresponding white lines (b, d, f) of the Ti/steel system sample with the coating thickness of 5 μm before treatment (a, b) and samples with the coating thickness of 2.5 μm (c, d) and 5.0 μm (e, f) treated by CPF.

in pearlite grains (α -Fe + Fe₃C) after treatment. The initial steel structure is a mixture of ferrite and pearlite grains. During a CPF impact (or any heating at the temperature greater than 1000 K) pearlite transforms to austenite. The recovery to the initial structure does not take place because of a high cooling rate.

The change of the phase composition and quenching effects result in the microhardness increase (Figure 4). The treated samples with the titanium concentration up to 8 at.-% showed 1.6 times microhardness increase in comparison with the untreated steel sample. Microhardness of these samples does not almost depend on the indentation depth (the curves c and d in Figure 4). The supersaturated α -Fe(Ti) solid solution is the only phase that can be seen in diffraction patterns of these samples (except for TiO₂ diffraction lines having a very small intensity). Thus, solid solution hardening seems to be the main hardening mechanism for samples with the Ti concentration up to 8 at.-%. At the same time no difference between the microhardness value of samples containing 4 and 8 at.-% was found. It can be connected either with small microhardness sensitivity to lattice distortion in this concentration range or with the action of other factors that were not revealed in the experiment.

The TiN phase formation causes the microhardness increase up to 5.5 GPa at a smaller indentation depth (the curves e and f in Figure 4) due to dispersion hardening in the thin surface layer. The increase of the Ti concentration up to ~30 at.-% leads to the formation of Fe₂Ti precipitates in the

mixed layer, providing a further microhardness growth in the bulk (3.8 GPa at the depth of 4.5 μm for the curve f in Figure 4). Thus, solid solution hardening and dispersion hardening can be the main mechanisms of the mixed layer microhardness increase.

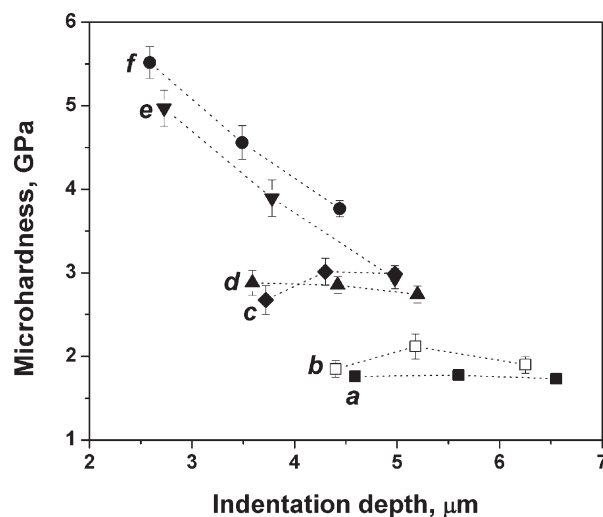


Figure 4. The microhardness dependence on the indentation depth of the initial steel sample (a), the Ti/steel system sample with the coating thickness of 2.5 μm before treatment (b) and the samples of the Ti/steel system with the coating thickness of 0.5 μm (c), 1.2 μm (d), 2.5 μm (e) and 5.0 μm (f) treated by CPF.

Conclusion

The coating thickness in a 'coating/substrate' system subjected to CPF treatment is one of the main parameters influencing the element and phase composition of a modified layer. Its variation results in the change of the alloying element concentration and hence the properties of an alloyed layer. Such an approach allows to increase the alloying element concentration and enlarge a range of alloys that can be synthesized.

Treatment of the 'Ti/steel' system by CPF resulted in the formation of the mixed layer with a different concentration of titanium depending on the initial coating thickness. The maximum titanium concentration obtained was 30 at.-% if the system with the coating thickness of 5.0 μm was treated. The increase of the titanium content was accompanied by the following phase transitions: $\alpha\text{-Fe} \rightarrow \text{supersaturated } \alpha\text{-Fe(Ti)} \rightarrow \text{supersaturated } \alpha\text{-Fe(Ti)} + \text{Fe}_2\text{Ti}$. The TiN formation in the thin surface layer was found for the systems with the coating thickness of 2.5 and 5.0 μm . The thickness of the mixed layer was found to be dependent on a coating material.

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