

# Steel surface TiCrN, TiMoN coatings structural phase state change features after low-energy alpha particles irradiation

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**Abstract.** The low-energy alpha particles irradiation impact on structural phase composition and 321S31 steel surface TiCrN and TiMoN coatings morphology have been summarized. The samples irradiation has been carried out in the DTs-60 (the Dubna cyclotron) heavy-ion accelerator by the  $^4\text{He}^{+2}$  low-energy ions (40 keV) into a  $1.0 \cdot 10^{17}$  ion/cm<sup>2</sup> fluence. It has been established that the 321S31 steel alpha particles implantation having energy of 40 keV results in the austenite initial  $\gamma$ -structure partial transfer, stimulated by the irradiation, to the martensite  $\alpha$ -structure. The low-energy alpha particles irradiation within the fluencies range from  $10^{16}$  to  $10^{17}$  ion/cm<sup>2</sup> for the TiCrN and TiMoN coatings formed by the ionic bombardment condensation method doesn't result in the phase transfers with a coating crystal lattice type change.

## 1. Introduction

Now days the great efforts are directed at obtaining the more powerful reactor facilities [1]. These reactor facilities product life must be equal to 60 years. This product life increasing is accompanied by a thermal and irradiation embrittlement damaging effect increasing. There are various methods to compensate this effect, such as the steels using with the higher thermal and irradiation embrittlement resistance; the neutrons flow decrease during operation; the products metal shortness initial critical temperature reduction; the using of coatings on a reactor body side on the basis of ceramics [2, 3]. For the final method using, it's necessary to produce the special coverings, had high physic-mechanical properties and used for the main material protect from the irradiation, thermal and other influences. Often the transition metals nitrides are used as coatings [4, 5]. These compounds combine ceramics and metal properties and have increased hardness, wear resistant and corrosion stability, thermal stability [6–8]. The transition metals TiCrN, TiZrN, TiMoN and other nitrides coatings are considered



to be perspective as protective coatings [9, 10]. However these covering properties stability problem under the irradiation influence is not sufficiently explored [9–12].

The investigations results of the TiCrN and TiMoN coatings surface structural-phase composition and morphology changing caused by the alpha particles irradiation modeled the transmutative helium accumulation in the nuclear reactors constructional materials are presented in this paper.

## 2. Samples and investigation methods

### 2.1. The covering production method

The coverings based on Ti-Cr-N have been applied on a carbon steel substrate surface (< 0.2 %) by the vacuum arc condensation method with the ionic bombardment (CIB). The substrates are capacitance discs 15 mm in diameter and 1 mm wide. The vacuum deposition modes have been the following: Ti and Cr cathodes, nitrogen residual pressure ( $P_N = 10^{-1}$  Pa), stress shear 60 V, cathode current 100 A, deposition time 60–120 s. As result the samples series 50–150 mm wide with the TiCrN coatings with the approximately equal titanium and chromium content have been obtained. The coatings deposition procedure is set out in great detail in [6, 8] papers.

The Ti-Mo-N coatings have been also formed by the CIB method at the titanium and molybdenum flows combination under a nitrogen residual atmosphere. The 321S31 steel plates with dimensions of 15×15×1 mm have been used as a substrate. Before the deposition the substrate surface ionic bombardment have been studied by titanium ions for 60 s, at potential on the substrate 1 kV, at titanium cathode arc current 100 A and at pressure within the chamber  $10^{-3}$  Pa, that gave the surface cleaning and its heating to a temperature of 450–500 °C. The coatings have been deposited in N<sub>2</sub> gas ambient at pressure  $10^{-1}$  Pa within the chamber, at potential on the substrate is equal to 120 V and at the titanium and molybdenum cathodes arcing currents 100 A and 180 A, respectively. The titanium and molybdenum plasma flows combination have been made by two cathodes allocation at an angle of 60° to each other at a distance equal to 120 mm from the substrate. As a result the samples series with the TiMoN coatings 2 μm wide have been formed.

The X-ray diffraction analysis has been made on the basis of a BRUKER company D8 ADVANCE diffractometer with using the copper radiation with the diffracted beam monochromator in Bragg-Brentano survey geometry. In some cases the survey in X-ray beam small-angle drop geometry (at an angle of 2°) within the angles range  $20^{\circ} \in 30^{\circ} \div 46^{\circ}$  has been used.

### 2.2 Alpha particles low-energy irradiation

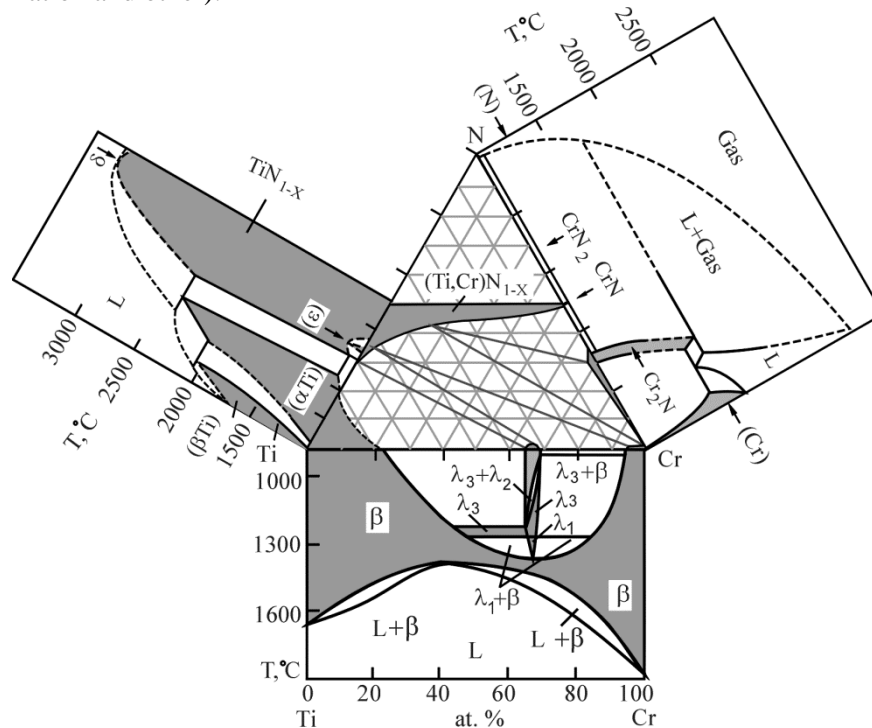
The low-energy alpha particles irradiation has been carried out on the basis of a DTs-60 (the Dubna cyclotron) heavy-ion accelerator low-energy channeling ECR (electron cyclotron resonance) at the Nuclear Physics Institute branch in Astana. The  ${}^4\text{He}^{+2}$  ions energy was 40 keV (20 keV/charge). The selected irradiation fluencies were between  $1 \cdot 10^{16}$  and  $5 \cdot 10^{17}$  ion/cm<sup>2</sup>. The irradiated surface square was 10 mm<sup>2</sup>. The irradiation temperature didn't exceed 150 °C.

According to the calculations (under the SRIM program) the 321S31 steel alpha particles projective range having energy of 40 keV is approximately 150 nm, the 321S31 steel straggling is approximately 75 nm, the TiCrN projective range is approximately 190 nm, the TiCrN straggling is approximately 83 nm, the TiMoN projective range is approximately 150 nm, the TiMoN straggling is approximately 80 nm. Therefore the implanted helium accumulates at the covering-substrate boundary in the carbon steel TiCrN coating samples. The implanted helium accumulates in the coating in the TiMoN samples.

## 3. Ti-Cr-N system structural phase states

In the Ti-Cr-N system the chromium and the titanium are related to transition metals [13, 14]. The titanium with the chromium in the liquid state are indefinitely soluble in each other. At the temperature decrease the alloys crystallize with forming a  $\beta(\text{Ti,Cr})$  solid solutions continuous series (Figure 1). The main transformations occur in the solid state. The intermediate stages with the Laves phase structure form near the TiCr<sub>2</sub> composition.

The Cr-Ti-N system third element (nitrogen) significantly differs by chemical properties from the metals, forming this compound. The nitrogen with transition metals can form compounds with an ordered structure. These compounds form from the solid solutions and can produce the variable composition phases. The phases and different polymorphic transformations wide variety also exists in the nitrogen compound with the titanium and the chromium [13]. This is caused by these compounds chemical bond various character. The existing typically metallic bond in the metals solid solutions with the nitrogen in some phases and compounds begins to move in a covalent and an ionic bond. Also the bonds intermediate types manifestation is discovered (metallic and covalent combination, covalent and ionic combination and other).



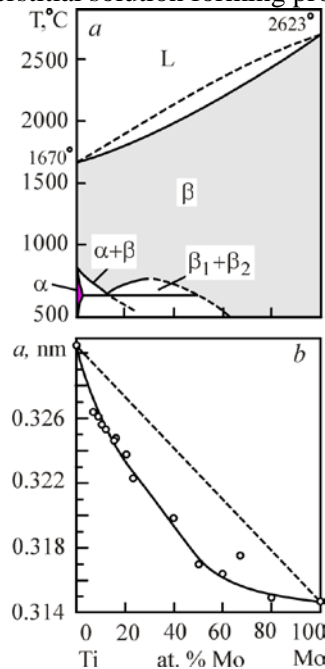
**Figure 1.** Cr-Ti, Cr-N, Ti-N systems binary diagrams [13] and Cr-Ti-N ternary system isothermal cross section at 1000 °C [14]. The single-phase areas are filled with grey color.

The TiN and CrN nitrides are fully mutually soluble and form solid solutions continuous series (Figure 1). The  $(\text{Ti,Cr})_x\text{N}_{1-x}$  ternary compound homogeneity region is wide. The TiN, CrN and  $(\text{Ti,Cr})\text{N}_{1-x}$  nitrides have the B1 cubic structure (NaCl prototype). The  $\text{TiN}_x$  compounds are related to the wide homogeneity region unordered nonstoichiometric nitrides group [15]. In  $\text{TiN}_x$  compounds the Ti atoms forms metallic face-centered cubic sublattice may containing N interstitial atoms or vacancies in its octahedral interstices. The nonstoichiometric disordered compound crystal structure type saving at the structural vacancies concentration change causes the homogeneity region presence. In our case the CrN nitride narrow homogeneity region means that the structural vacancies appearance leads to the crystal structural type change.

#### 4. Ti-Mo-N system structural-phase state

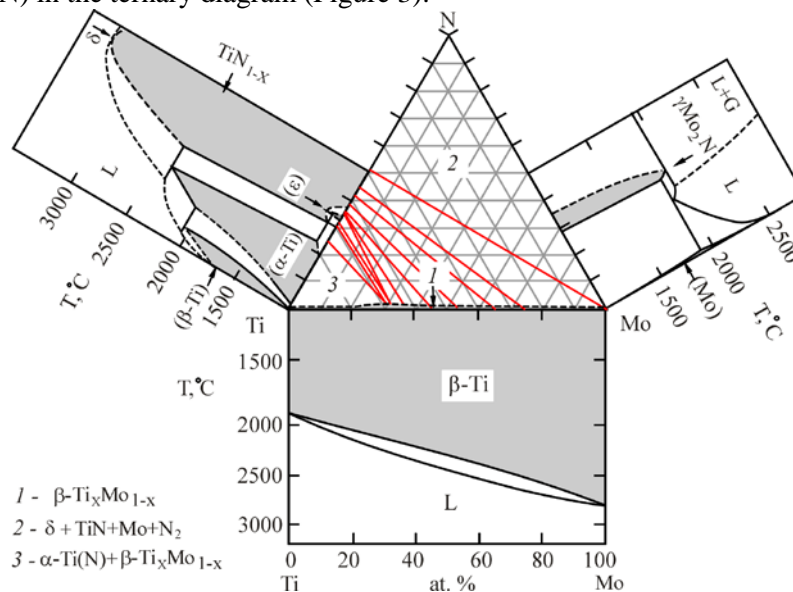
There are the solid solutions continuous series in the Ti-Mo system ( $\beta$ -Ti,Mo) (Figure 2a). The titanium alloying by the molybdenum leads to the  $\alpha \rightleftharpoons \beta$  polymorphic transformation temperature decrease. You can see at the presented diagram (Figure 2a) that the solid solution decomposition occurs to  $\beta_1$  and  $\beta_2$  solid solutions and the phase separation area are asymmetrical and shifted to the Ti side. The Mo solubility in the ( $\alpha$ -Ti) is weak and isn't above 14 % (at.) at the monotectoid transformation temperature.

A significant negative departure from the Vegard law is found in a ( $\beta$ -Ti, Mo) solid solution  $a$  lattice parameter concentration dependence (Figure 2b), reflecting the strong lattice compression and as a consequences should results in interstitial solution forming problem. It really happens (Figure 3).



**Figure 2.**The Mo–Ti system state diagram (a) and the solid solution lattice parameter concentration dependence (b) [13].

You can see in the ternary constitutional diagram that the nitrogen atoms solubility in the solid solution ( $\beta$ -Ti, Mo) is very limited and it happens in a very ternary compound narrow homogeneity region ( $\beta$ -Ti, Mo, N) in the ternary diagram (Figure 3).



**Figure 3.** The Mo-Ti, Mo-N, Ti-N systems binary diagrams [13] and the Mo-Ti-N ternary system isothermal cross-section at the 1000  $^{\circ}\text{C}$  [14]. The single-phase regions are indicated by grey color.

There are a few molybdenum nitrides in the Mo-N system [13]. There are a high temperature  $\gamma$ -Mo<sub>2</sub>N (L'1 structure type, Fe<sub>4</sub>N prototype) and a low temperature  $\beta$ -MoN<sub>2</sub> (L'6 structure type) in the Mo<sub>2</sub>N composition region. The nitride in the  $\delta$ -MoN forms in the composition area at 50 % (at.) N with the hexagonal syngony ( $P6_3/mmc$ ,  $B_h$  structure type) and is unstable at the high temperatures.

The Mo-Ti, Mo-N, Ti-N systems binary diagrams [13] and the Mo-Ti-N ternary system isothermal cross-section at the 1000 °C are presented in Figure 3 [14]. The presented Mo-Ti-N ternary system isothermal cross-section at 1000 °C shows that Mo-Ti-N system ternary compounds practically don't form, except for  $\beta$ -Ti<sub>x</sub>Mo<sub>1-x</sub> solid solution narrow homogeneity region with the dissolved nitrogen little amount (region 1, Figure 3).

## 5. Results and considerations

### 5.1 The 321S31 steel

It has been established by the X-ray structure analysis method, that the steel in the initial state is two-phase with the  $\gamma$ -Fe content to 85 % on the base of the fcc lattice and  $\alpha$ -Fe content about 15 % on the basis of the bcc lattice. The irradiation by using of the low energy alpha-particles to the fluence of  $1 \cdot 10^{17}$  has been led to the  $\alpha$ -phase content increasing in the steel to approximately 25 %. Consequently the  $\gamma$ -Fe content has been increased to 75%. Therefore, the irradiation by using the low energy alpha-particles leads to the significant 321S31 austenitic steel structural-phase state change caused by the irradiation through an austenite-martensite phase transition [11].

### 5.2 The TiCrN coating on the carbon steel

According to [6], Ti-Cr-N coatings, deposited on the metal substrate by using the CIB method at temperatures 450 °C – 500 °C, are the solid solution (Ti, Cr)N with the fcc lattice. The TiCrN coatings formed by using the plasma flows condensation, having titanium and chromium atoms, in nitrogen atmosphere, are the phases mix having the content range from (Ti, Cr)N + Cr to TiN + (Ti,Cr)N with the relative concentrations increasing of the titanium to the chromium. This means that the chromium content increasing leads to the phases mix formation in the covering, such as (Ti, Cr)N solid solution and Cr, and the titanium content increasing leads to the other phases mix formation, such as (Ti,Cr)N solid solution and TiN. The elements content analysis made by means of the energy dispersed X-ray microanalysis (EDXM) has been shown that the coating is the titanium, chromium and nitrogen composite with the titanium and chromium content of  $52.51 \pm 0.07$  at % and  $47.49 \pm 0.07$  at % respectively. The substrate consists of 99 at. % Fe, 0.6 at.% Cr and 0.4 at.% Si. Complementary Bragg reflexes weren't indicated by the steel samples X-ray investigations with the coating on the base of TiCrN. May be this is caused by the small coating thickness (50÷150 nm). The alpha-particles ions irradiation having energy of 40 keV to the fluence of  $1 \cdot 10^{17}$  ion/cm<sup>2</sup> has been led to some diffraction pattern change. The background has been significantly increased. The reflexes from the bcc lattice plates have became wide and the weak reflexes occur on the irradiated samples diffraction pattern at the angles are equal to 37° and 62°. The analysis showed that complementary reflexes relate to the (Ti,Cr)N<sub>1-x</sub> compound with the B1 cubic structure.

Thereby the carbon steel surface TiCrN coating irradiation by using of the helium ions leads to the structure defects formation. This causes the disordered nonstoichiometric (Ti,Cr)N<sub>1-x</sub> nitrides formation with the B1 structure [15].

### 5.3 The 321S31 steel TiMoN coating

It's established by using the X-ray analysis method that the near-surface layer generally consist of the  $\delta$ TiN titanium nitride (cubic syngony with the Fm-3m space group, NaCl prototype) and a ( $\beta$ -Ti,Mo) solid solution little amount. It's established that the  $\delta$ TiN titanium nitride lattice parameter is equal to  $0.4298 \pm 0.0006$  nm. The ( $\beta$ -Ti,Mo) solid solution lattice parameter is equal to 0.3149 nm. As it's seen on the presented ( $\beta$ -Ti,Mo) solid solution lattice parameter concentration dependence, the Mo alloying by using the titanium to 20 at.% only slightly change the lattice parameter (Figure 2b).

The X-ray photography using in the grazing beam geometry has allowed indicating the ( $\beta$ -Ti, Mo) solid solution weak reflexes. Besides the ( $\beta$ -Ti, Mo) solid solution content isn't uniform along the coating thickness and increases with the distance increasing from the surface.

The low energy alpha-particles irradiation to the fluence of  $1 \cdot 10^{17}$  hasn't been led to the significant diffraction pattern change. As well as to the irradiation, the ( $\beta$ -Ti, Mo) solid solution,  $\delta$ TiN titanium nitride and alpha-phase compound reflexes have been indicated from the steel substrate.

## 6. Summary

The low energy alpha-particles irradiation influence on the 321S31 steel and TiCrN and TiMoN coatings surface crystal structure and morphology by using the  $10^{16} - 10^{17}$  ion/cm<sup>2</sup> fluences is investigated by using the X-ray analysis method, scanning electron and atom-power microscopy.

It's presented that in the 321S31 steel the alpha-particles implantation having energy of 40 keV leads to the austenitic initial  $\gamma$ -structure partial conversion into martensite  $\alpha$ -structure caused by the irradiation. The  $\gamma \rightarrow \alpha$  transformation rate depends on the irradiation fluence, i.e. the helium supersaturation rate in the straggling region, reflecting ions ranges dispersion in the ion stopping region, i.e. in the projective range region. For the TiCrN and TiMoN coatings formed by using the ionic bombardment condensation method the low energy alpha-particles irradiation within the fluence range from  $10^{16}$  to  $10^{17}$  ion/cm<sup>2</sup> doesn't lead to the phase conversions with the crystal lattice type change.

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