UDC 621.785; 669.017:669.15

L. I. Fedorenkova*, S. N. Antropov, G. V. Zinkovsky

Oles Honchar Dnipropetrovsk National University, Dnipro, Ukraine
**e-mail: Luba.Fed@gmail.com*

FEATURES OF DIFFUSION LAYER ON TITANIUM SURFACE OBTAINED IN BORON-CONTAINING MEDIUM

The features of diffusion layer formed on the Ti samples of BT-0 grade in the B-medium, by processing in electrolyte plasma, and in a combined way are studied. Metallographic analysis shows the character of microhardness changes with depth depending on saturation conditions, and X-ray diffraction analysis proves high-B compounds forming at a distance of 10-40 μm to surface. As the B concentration decreases with depth, the formation of compounds mainly of Ti_2B, Ti_3B_4, and Ti_2B_5 types occurs. Here the distribution of borides is due to sample saturation mode and the metal structure, into which B diffuses. For the saturation process in electrolytic plasma, the local heating of the surface and diffusion process under non-equilibrium conditions are typical. At the combined treatment, a structure of the diffusion layer formed under such conditions transits from a metastable state to the stable one. The calculated dependences of B concentration on depth, according to the temperature changes of diffusion coefficient, agree with experiments. The treatment in electrolyte plasma forms the diffusion layer with nanosized Ti boride inclusions, at grain boundaries mainly, which leads to surface dispersion hardening. Getting the wear-resistant coatings on Ti containing Ti-B phases improves efficiently the safety and reliability of power plants for various purposes, including nuclear ones.

Keywords: electrolytic plasma, treatment, microhardness, diffusion layer, nanosized inclusions.

Досліджено особливості дифузійного шару, який сформовано на зразках Ті марки ВТ-0 у бормістячому середовищі, обробкою в електролітній плазмі та комбінованим способом. За металографічним аналізом, характер зміни мікротвердості з глибиною залежить від умов насичення, а за пошаровим рентгеноструктурним – високоборисні сполуки утворені в 10 - 40 мкм від поверхні. Зі зменшенням концентрації В із глибиною відбувається переважно утворення сполук типу Ti_2B, Ti_3B_4, Ti_2B_5. Розподіли боридів обумовлені тут режимом насичення зразків та структурою металу, в який дифундує В. Характерними для процесу насичення в електролітній плазмі є локальний розігрів поверхні, дифузія в нерівноважних умовах. За комбінованої обробки відбувається перехід структури шару, сформованого в зазначених умовах, з метастабільного стану в стабільний. У залежності коефіцієнта дифузії від температури проведено розрахунки розподілу В за глибиною, що збігаються з експериментами. Обробка в електролітній плазмі дає дифузійний шар з нанорозмірними включеннями боридів титану переважно по межах зерен, що веде до дисперсійного зміцнення поверхні. Зносостійкі покриття на Ті з Ті-В фазами – ефективно підвищать безпеку і надійність енергосистем різного цільового призначення, ядерних включно.

Ключові слова: електролітна плазма, обробка, мікротвердість, дифузійний шар, нановключення.

Изучены особенности диффузионного слоя, сформированного на образцах Ті марки ВТ-0 в борсодержащей среде, при обработке в электролитной плазме и комбинированным способом. Из металлографического анализа, характер изменения микротвердости по глубине задают условия насыщения, а из послойного рентгеноструктурного – высокобористые соединения образуются в 10 – 40 мкм от поверхности. С убыванием концентрации В по глубине образуются соединения, в основном, типа Ti_2B, Ti_3B_4 ,Ti_2B_5. Распределения боридов тут обусловлены режимом насыщения образцов и структурой металла, в который диффундирует В. Процесс насыщения характерен в электролитной плазме локальным разогревом поверхности, неравновесным ходом диффузии. Комбинированная обработка ведет к переходу структуры диффузионного слоя, формируемого в указанных условиях, из метастабильного состояния в стабильное. В зависимости коэффициента диффузии от температуры рассчитаны распределения В по глубине, согласующиеся с опытом. Способ обработки в электролитной плазме дает диффузионный слой с наноразмерными включениями боридов титана, в основном, по границам зерен, вызывая дисперсионное упрочнение поверхности. Износостойкие покрытия на Ті с Ті-В фазами – эффективно повысят безопасность и надежность энергосистем различного назначения, в том числе ядерных.

Ключевые слова: электролитная плазма, обработка, микротвердость, диффузионный слой, нановключения.

1. Introduction

Interest for borides is unabated and now even more importance is given to the development of production technology, with not only traditional, but also non-carbon nanomaterials and nanoceramics [1]. It is known that titanium and its alloys have many superior mechanical properties and insufficient wear-resistance, but boride modification of surface layers [2] substantially removes scuffing and improves operational properties of such alloys [3]. However, the Ti-B systems as well as physical properties of such phases are still poorly understood.

In this research we investigated characteristics of diffusion layer formed on titanium samples of VT-0 grade in the boron-containing medium under a treatment in electrolyte plasma and by combined method.

2. Materials and methods

Titanium samples of VT-0 grade were studied after the treatment in the following ways:

1) in an aqueous electrolyte solution according to the method of plasma discharge [4];
2) by the combined method with an aqueous electrolyte solution, followed by the treatment with a boron-containing powder mixture at temperatures of T = 950 - 1000°C for t = 3 hours.

The microstructure of the treated samples was showed up by etching in 0.5% HF-solution. The metallographic analysis of the samples was performed with a microscope "Neophot-21" and microhardness tester “PMT-3” under a load of 50 g. The identification of phase components of diffusion layer was carried out by X-ray diffraction analysis (DA) with a diffractometer “DRON-2” in the iron and copper radiation.

3. Results and discussion

The thermochemical treatment (TT) results in diffusion layer on Ti surface with a microstructure as shown in Fig. 1:

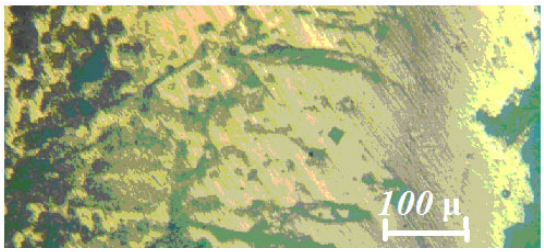
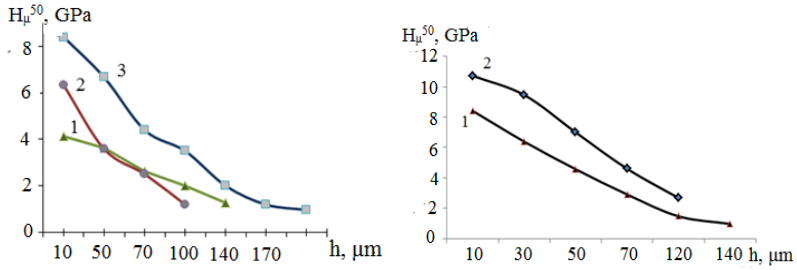


Fig. 1. Microstructure of titanium sample after the TT in the boron-containing medium, ×1000

By changing the value of indenter (Fig. 1), it is possible to conclude about the micromechanical features of layer. From the graph shown in Fig. 2 a, the character of microhardness change with sample depth depends on the saturation conditions. With increasing current density ***j*** and treatment duration ***t*** the layer microhardness rises. Fig. 2, b shows the change in microhardness with layer depth for samples, one of which is treated with a combined method. In the last case the microhardness takes greater values. The micromechanical characteristics of a layer are affected, above all, by the phase composition of layer. A feature of the treatment with electrolytic plasma [5] is that due to saturation, there are several modifications of borides in the diffusion layer. According to the layer-by-layer DA, high-boron compounds are formed at a distance of 10-40 µm from the surface (Table 1).



a b

Fig. 2. Microhardness dependence on the diffusion layer depth for Ti treated: a) in modes: 1 – *U*=60-65V, *j*=0.2-0.7 A/cm^2, *t*=15 min; 2 – *U*=60-75V, *j*=0.2-0.3 A/cm^2, *t*=25 min; 3 – *U*=70V, *j*=0.6-1.1 A/cm^2, *t*=60 min; b) 1 – electrolytic plasma in a mode *j*=0.13-1.3 A/cm^2, *U*=25-45 V, *t*=18 min; 2 – combined treatment in electrolytic plasma, followed by TT in coating with B amorphous powder and Al at 1223K for 3 hours.

Table 1

Distribution of titanium borides in the depth of diffusion layer at layer-by-layer X-ray DA

Depth of diffusion layer, μm	Phase combination
5-10	Ti_2B, TiB_2, TiB
10-40	TiB, Ti_2B, Ti_3B_4
40-80	Ti_2B, Ti_3B_4, Ti_2B_5

Boron concentration decreasing with the sample depth leads to the formation of compounds of the types Ti_2B, Ti_3B_4, Ti_2B_5. The feature of the distribution of borides with the metal depth is due to the saturation mode of the samples and the metal structure, in which boron diffuses. It should be noted, that the presence of dislocations and cracks in a sample serves as additional boron concentrators and boron distribution undergoes abnormal bursts in these places. There high-boron phases can be formed due to boron liquation.

For the saturation process in electrolytic plasma, the local heating of surface and the diffusion flow under non-equilibrium conditions are typical. Local temperature can reach more than 1273 K. In places where the temperature is the highest, the diffusion of boron is more intense [6]. According to calculations of temperature distribution with the sample depth, the maximum temperature fits to the volume diameter of 1.0 – 1.2 μm [5]. Beyond this size range the temperature decreases sharply and, according to experimental data [6], the average for the metal surface, depending on the treatment conditions, is from 373 K to 600 K. Under these conditions there is such dependence of the diffusion coefficient:

$$D = D_0 \, exp\{- Q/(RT)\}, \quad (1)$$

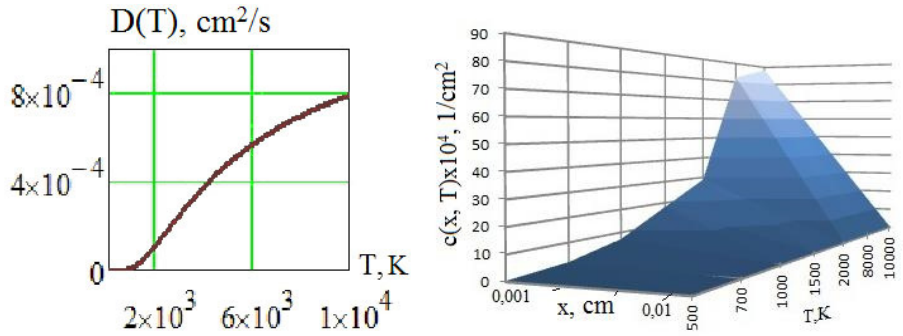
where D_0 is a pre-exponential factor directly related to the number of particles involved in a jump to overcome the barrier height; Q is activation energy, J/mol; T is absolute temperature, at which diffusion occurs, K; R=8.31 J/(K mol) is the universal gas constant.

According to Frenkel-Brown [8, 9], there is a relation $D_0 = a^2/(6\tau_0)$, where a stands for a lattice constant, Å= 0.1 nm; $\tau_0 = 1/\nu$ – the time of one oscillation, s; ν – the maximum frequency of atom oscillation, 1/s. The calculation results in the value D_0 =0.0013 cm^2/s.

To determine the activation energy, we use the theory by Brown, according to which heat losses $Q=3b^2RT_{mm}$, where T_{mm} is metal melting point, K; b is a constant, close to unity. Taking this into account, the equation (1) gives

$$D = D_0 \, exp(- 3b^2T_{mm}/T). \quad (2)$$

According to the phenomenological description of diffusion processes by Onsager [7], in these conditions the diffusion occurs under the simultaneous action of thermodynamic and electrical forces. The action of such forces causes a diffusion transfer of *i*-th varieties in a multicomponent system. Atoms come in a directional move at an average speed $\langle v_i \rangle_F = U_i F_i$, where U_i means mobility, i.e. the speed that the particles acquire at the driving force, $F_i = -kT\nabla l\, n\, \gamma_i$ – power transmission effect on flow of own potential field gradient of crystal, which moves diffusing atom, γ_i – activity coefficient. The result is the diffusion flux with density: $j_i = c_i\langle v_i \rangle_F = c_i F_i U_i = -c_i\, U_i \nabla \mu_i$. For a real solution: $j_i = -D_i \nabla c_i + c_i \langle v_i \rangle_F$. Given the above, the calculations result in graphs of boron diffusion coefficient changes with temperature and in the depth distribution of boron concentration in the sample (Fig. 3). The graph shows that the boron diffusion coefficient is about 10^{-4}cm^2/s and increases with the growth of local temperature; when entering the temperature range above $1.5 \cdot 10^4$ K, it stops changing. The distribution of boron concentration with layer depth agrees with the experimental data [6].



a b

Fig. 3. a) Dependence of diffusion coefficient on the temperature at saturation of titanium with boron; b) The boron concentration changing with the sample depth (the dependence *D(T)* is taken into account).

At the electrolyte plasma conditions, titanium borides are formed mainly as nanoscale and microcrystalline inclusions, which are irregularly distributed across the layer depth. At the combined treatment, the structure of diffusion layer formed in the non-equilibrium plasma electrolytic conditions, transited from a metastable state to a stable one. This transition is accompanied by the formation of new phases and the redistribution of diffused elements.

4. Conclusions

The diffusion layer, formed on titanium surface by treatment in electrolyte plasma, contains the nanoscale titanium boride inclusions, which are concentrated mainly at grain boundaries and provide dispersion strengthening of surface. At the combined treatment, the structure of diffusion layer, formed in the non-equilibrium conditions of electrolytic plasma, transits from a metastable state to the stable one. Given the dependence of diffusion coefficient on temperature, the distribution of boron calculated along the sample depth agrees with experimental results. Producing the wear-resistant Ti coatings that include Ti-B and oxygen-titanium-boron-containing phases is one of the possible ways of solving urgent problems of safety and reliability of many power plants, including nuclear ones.

References

1. **Krishnamoorthy, S.** Nanomaterials: A Guide to Fabrication and Applications (Devices, Circuits, and Systems) / Sivashankar Krishnamoorthy // L-NY: CRC Press, – 2015. – 312 p.

2. **Atar, E.** Friction and Wear Behaviour of Borided Ti_6Al_4V Alloy Sliding Against Al_2O_3 and Si_3N_4 Balls in Water [Text] / E. Atar, E. S. Kayali, H. Cimenoglu // Defect and Diffusion Forum.– 2011.– Vols. 312-315.– P. 1004-1009.

3. **Kaplan, Y.** An experimental study on wear behavior of boronized Ti_6Al_4V alloy under dry and wet sliding conditions [Text] /Y. Kaplan, A. C. Can, A. Ulukoy // Proc. Turkeytrib'15 – 1st Int. Conference on Tribology, 7-9 Oct 2015 Istanbul-Turkey - Istanbul: 2015.

4. **Fedorenkova, L. I.** Sposib boruvannya alyuminiyu ta yogo splaviv [Text] / L. I. Fedorenkova, I. M. Spiridonova, S. B. Pylyaeva // Patent UA №43482 - 15.04.2004. – No 4.

5. **Fedorenkova, L. I.** Osobennosty dyffusyonnogo sloya, sformyrovannogo pod deystviem elektrolitnogo razryada [Text] /L. I. Fedorenkova // Visnyk DNU. Physics. Radioelectronics. – 2012. – № 2. – Vol. 20. – P. 87 - 93.

6. **Fedorenkova, L. I.** Investigation of the saturating with boron of aluminum and its alloys in aquous solution of electrolyte [Text] / L. I. Fedorenkova, I. M. Spiridonova // Visnyk DNU. Physics. Radioelectronics. – 1998. – Vol. 3. – P. 10 - 18.

7. **Manning, J. R.** Diffusion kinetics for atoms in crystals [Text] / J. R. Manning // Princeton: Van Nostrand, – 1968. – 257 p.

8. **Freydlin, M. G.** Strukturnie osobennosti sloyev, poluchennih pri elektroiskrovom legirovanii titanovih splavov [Text] / M. G. Freydlin i dr.// Elektronnaya obrabotka materialov. – 1986. –No 2. – P. 26-28.

9. **Zayt, V.** Diffuziya v metallah [Text] / Pod red. B. I. Boltasa // M.: IL, – 1958. – 247 p.

Received 15.05.2016.