Structure and properties of titanium, alloyed by oxygen

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Abstract.

In this work the possibility of using of the gaseous oxygen as alloying component in process of chamber electroslag remelting (ChESR) of titanium sponge is considered. The oxygen is concerned to list of main admixtures of technically clean titanium, which provide the essential influence on its properties. However in contrast to nitrogen and hydrogen it renders not only negative, but also positive influence on titanium properties. Increase the contents of the oxygen brings about increasing of strength, hardness but reduction of the plasticity of titanium. Controlling its contents in metal in determined degree, it is possible to reach the optimum correlation between the plastic and strengthening characteristic of the titanium alloy. The oxygen it is possible to consider as perspective alloying element to obtain new titanium alloy. This is particularly important for medical product, for which along with mechanical properties on the first plan go out corrosion stability and biocompatibility. In contrast to other alloying component (for instance, vanadium), the oxygen is more safe. The most economic expedient it is using the gaseous oxygen for alloying of titanium.

In this work the titanium samples with content of the oxygen from 0.035 to 0.27% were investigated, which got by alloying by oxygen directly from gas phase in process of chamber electroslag remelting of titanium sponge.

It is shown that hardness of the metal increases with increasing of the contents of oxygen. So, the maximal hardness is typical for samples with contents of the oxygen 0.27%wt., but minimal - for sample with contents of the oxygen 0.035%wt. At the same time, in radial direction the hardness remains approximately constant that is indicative of uniform distribution of admixtures on horizontal section of ingot.

The oxygen in titanium noticeably influences on the metal structure formation. So, for titanium with contents of the oxygen within from 0.053 to 0.110% coarse dendritic structure is typical, in which differences between separate area are revealed under small magnifications. Dendritic area etch evenly without clearly marked substructure. In some cases inside the dendritic areas weakly marked plate substructure is observed, typical to technically clean titanium in cast condition.

Increasing of the contents of the oxygen to 0.2% and above provides the forming of structure of the shear transformation, which promote the growth strength properties. The formation of such structures in cast titanium possible to explain increasing of the contents of the oxygen, which influence on kinetics of the phase polymorphic transformation in metal during cooling.

The results of the study of the structure and measurements of hardness have shown that ChESR provides good chemical and structural homogeneity of titanium ingots, alloyed by oxygen.

Introduction

The development of the scientifically - based branches of industry and energy saving technologies today is impossible without the use of new materials, possessing the raised level of properties. These are, first of all, high toughness, plasticity, strength and corrosion stability. These requirements are met by titanium and alloys on its base. In terrestrial crust there is approximately 0.6% of titanium. In terms of abundance it occupies the fourth place after aluminum, ferrum and magnesium. Additionally, it is necessary to note that Ukraine falls into the five of the largest producers of titanium in the world. Titanium is characterized by the combination of such valuable properties as small density, high level of specific strength, corrosion stability, cold-resistance, nonmagnetic character and some other valuable physical and mechanical features. Due to these, it is a base construction material for aircraft- and rocket production, energy generation, machine building, medicine and other high-tech industries. Recently the developers of new titanium alloys pay the special interest to medicine. These, first of all, are materials for different implantants. The need for such products all over the world is increased every year in geometric progression. In the same time the "medical" alloys must meet the special requirements, the main of which, except strength and plasticity, is biocompatibility. Such materials must be adapted in the organism of the person, not causing rejection, and possesses good physical, chemical and biological properties. Today, one of the main titanium alloy applied for these aims in medicine is the alloy BT6C (Grade5). However, it is necessary to note that the presence in it the alloying component of vanadium can bring about the harmful influence on the organism of a person, since it is known that the compounds of vanadium under the certain conditions can be toxic. So, it is important to alloy titanium by safe elements, in order to avoid the formation of harmful compounds for the organism of a person.

In this respect, the oxygen presents the certain interest, which for titanium is the reinforcing element. It is soluable both in $\alpha - Ti$ and in $\beta - Ti$ [1], forming interstitial solid solution. The maximum solubility of oxygen in titanium makes up about 30 at.%. The most observable influence upon the mechanical properties of titanium is that oxygen builds up its content in metal up to 0.6 % mass [2]. As a result there is the significant increase of strength features under comparatively low fall of plastic properties.

On this base we can make the conclusion that managing the contents of oxygen in titanium is possible to a considerable extent in order to influence upon its mechanical properties. In this respect it is necessary to note that the compounds of oxygen with titanium are harmless for a human organism and are used in pharmaceutics and medicine[3].

The given work is dedicated to study of the influence of the oxygen contents on structure and properties of titanium in as-cast, annealed and heat - treated conditions.

For obtaining titanium, alloyed by oxygen, the chamber electroslag remelting is used. This process successfully allows both to refine and to alloy titanium by different elements, including oxygen, getting its uniform distribution on height and cross section of ingots [4-7]. The process provides simultaneous melting of the metal consumable electrode, entering the alloying element and the ingot crystallization in the controlled atmosphere. As a result structural and chemical homogeneity of the obtained material is provided.

However, it is not enough to get the alloy with the given content of oxygen. The important questions are both the study of influence of the heat treatment on structure and properties of the metal and the development on this base the rational regime, which guarantees the availability of the given structure.

In the given work the object of the study was the alloy samples, cut from the ingots of titanium ChESR with different contents of oxygen (from 0.053 to 0.270% O).

The ingots were obtained by the method of the chamber electroslag remelting according to the methods, described below. The consumable electrodes for ChESR were made by the method of pressing of the titanium sponge produced by RE "ZTMC". The standard sponge of the TG100 grade with content of oxygen 0.035% (the melts № 3,4,7) and the sponge beforehand alloyed by oxygen [8] up to 0.11% (the melts № 1, 2, 5,6) were used. The pressed electrodes with the diameter 40 mm and length 600mm were melted down in the crystallizer with the diameter 60 mm. The refining was done in the chamber electroslag furnace, built on the base of the unit A-550. The construction, in addition, was equipped with the ballons with argon-oxygen mixture, as well as the device for controlling the consumption and pressure of gases. During melting the gas overpressure (up to 25 kPa) in the system for compensation of its possible losses was supported. The sources of the gaseous oxygen were argon of the first grade, containing 0.002% oxygen (all-Union State Standard 10157-79), and specially prepared argon-oxygen mixture (O_2=30%). The remelting was conducted under flux from pure CaF_2 of "Pure" grade and under flux CaF_2+Ca. The flux was melted directly in the crystallizer using the technology of the "hard" start. The start mixture was prepared from the titanium chips and the working flux. The electric parameters of remelting were supported at the rate of U = 40 V, I =2.0-2.2 kA., providing good quality of the surfaces of the melted ingots. The argon-oxygen mixture was given through the tubes in the sealed disk of the upper flange of the water-cooled crystallizer.

The parameters of remelting and contents of oxygen in the investigated ingots are provided in the table 1.

The structure was researched with using of the microscope Carl Zeiss "Axiovert 40 MAT" and "Neophot-21" with high-power microscopic image from 50 to 500. For the reason of studying the influence of the heat treatment on the structure and properties of the cast metal the annealing at the temperature 1100^0C with cooling in a furnace and tempering at the temperature 1100^{0}C with cooling in water were conducted. The holding at tempering was produced due to calculation rate 2 min. on 1 mm of the section. After annealing and tempering the samples were cleaned on the flat-polishing tool and hardness was measured on the device TC2 in the scales HRC, HRB and the measurements obtained were translated according to the table into HB.

It is necessary to note that under alloying titanium by the gaseous oxygen the increase of the nitrogen contents in metal up to 0.020 -0.030 % was observed. However it is within the requirements of the all-Union State Standard 19807-91 for titanium of the marks BT1-00 and BT1-0 (N up to 0.04%) and ASTM B-337 for the technical titanium of Grade1 -Grade 3 (N = 0.03-0.05%).

Table 1 Parameters of remelting and contents of oxygen in the investigated ingots

№	Electrode	Slag	Atmosphere in furnace	Content of oxygen,%
1	Titanium sponge alloyed by oxygen	CaF_2+Ca (2.5%)	Argon (the stagnant atmosphere)	0.110* 0.083
2	Titanium sponge , TG110	CaF_2	Argon (the running atmosphere)+ mixture of Ar +O_2	0.035 0.110
3	Titanium sponge , TG110	CaF_2	Argon (the stagnant atmosphere) (the top grade)	0.035 0.053
4	Titanium sponge , TG110	ANF-1	Argon (the stagnant atmosphere) (the top grade)	0.035 0.069
5	Titanium sponge alloyed by oxygen	CaF_2	Atmosphere: the running atm. – flushing by the mixture of Ar+O_2 under "max. consumption"	0.110 0.270
6	Titanium sponge alloyed by oxygen	CaF_2	Atmosphere: the running atm.- flushing by the mixture of Ar+O_2 under "min. consumption»	0.110 0.220
7	Titanium sponge , TG110	CaF_2	Atmosphere: the running atm.- flushing by the mixture of Ar+O_2 under "max. consumption	0.110 0.230

*- numerator – an initial content, denominator – after remelting.

Homogeneity of the metal was researched at the first stage in the as-cast condition by means of measurements of hardness in the radial direction.

On the figure 1 the graph of the distribution of hardness in the samples in the as-cast condition in the direction from the centre to the surface is given.

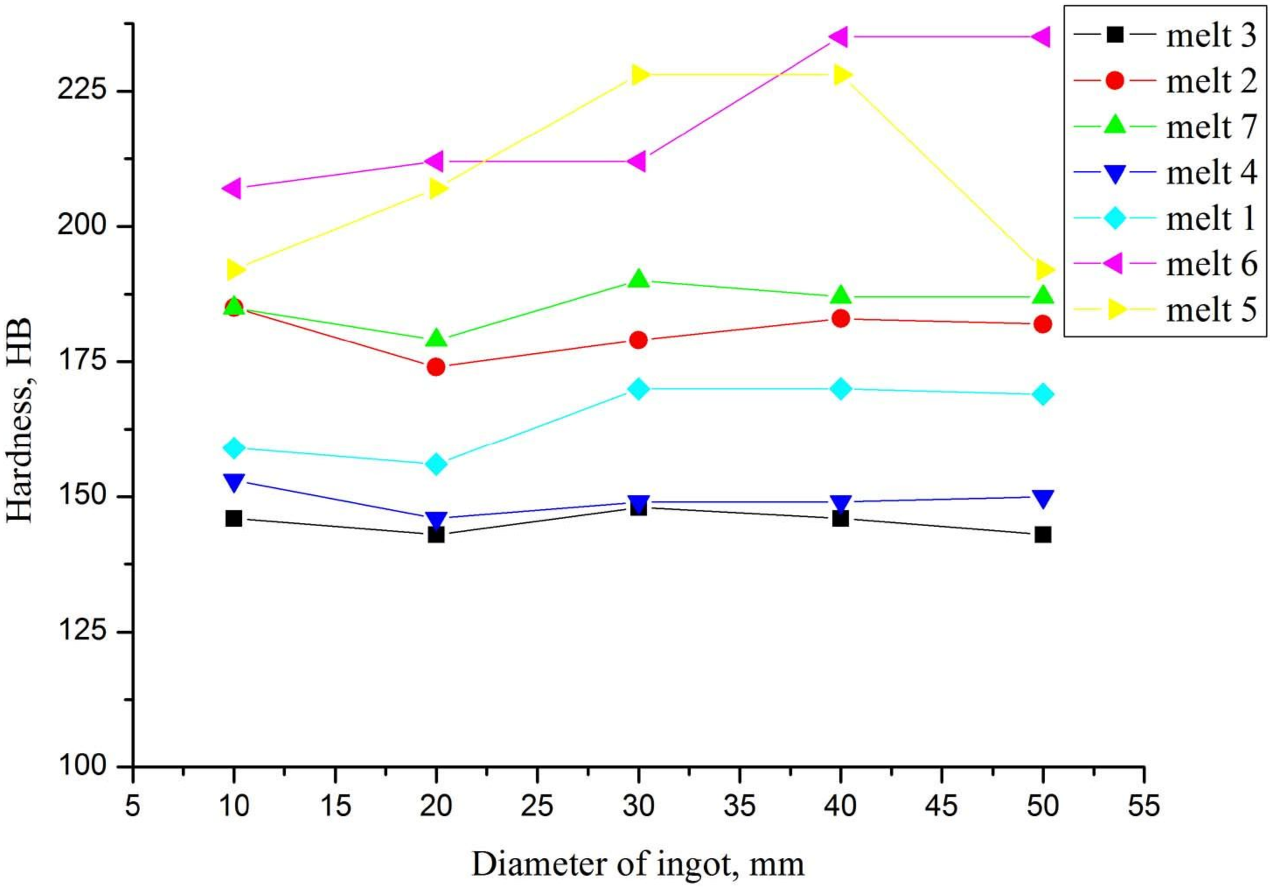
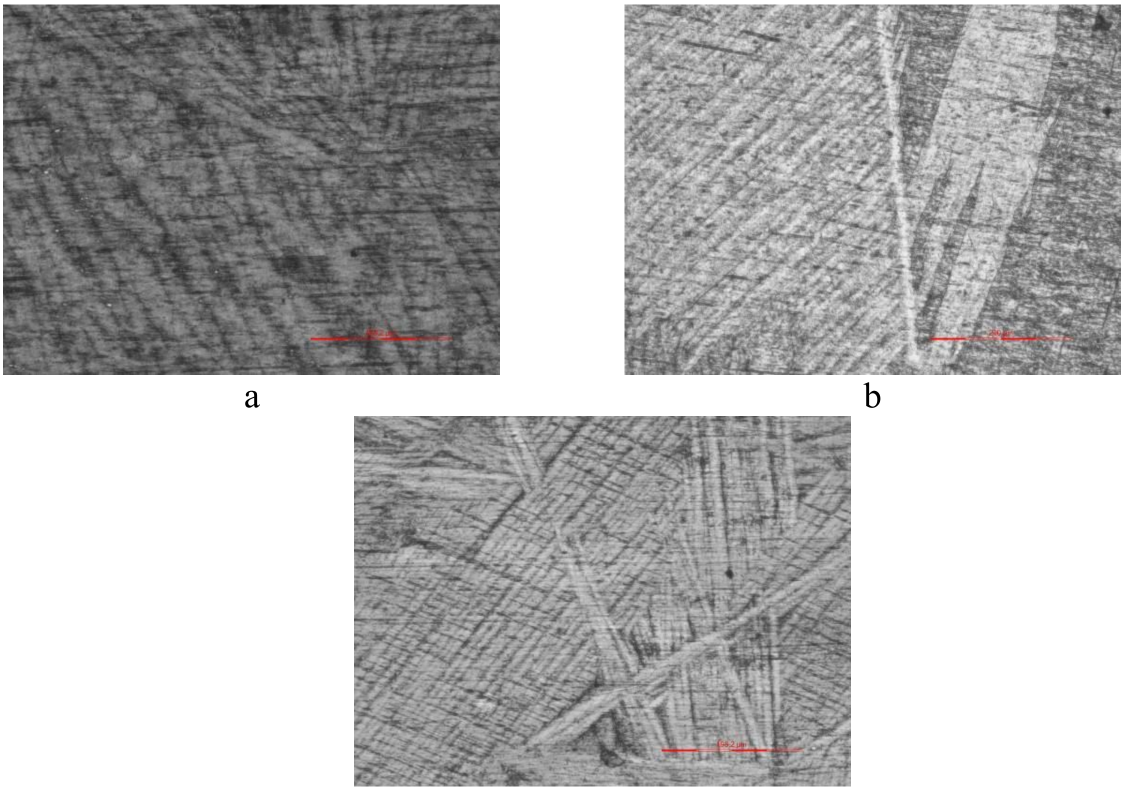


Figure 1 – Distribution of hardness on the radius of ingots

From the graphics it is seen that change of hardness on the section is changed with the change of the oxygen contents. Under the lowered oxygen contents, hardness is uniform on the sample section. When the oxygen content is increased, the even distribution falls. The maximum hardness (220-229 HB) is typical for the melt № 5 (the oxygen contents – 0.270), and the least one (138-145 HB) – for the samples of the melt № 3 and № 4 (the oxygen contents - 0,053 and 0,069).

The structure of titanium in the as-cast condition was studied at the second stage .

The structure of samples in the as-cast condition is given on the figure 2



a b

c

Figure 2 – Microstructure of the metal, x100: a-[O]=0.053%, the melt № 3; b-[O]=0.083%, the melt № 1; c-[O]=0.270%, the melt № 5

As it is seen from the figure 2 in the melts № 3, 1 and 5 the uniform single-phase structure is formed, however, its morphology depends on the oxygen content. The formation of the structure can be connected with the influence of oxygen on kinetics of the transformation. The equilibrium solubility of oxygen in β phase is more than in α phase that is why while cooling and $\beta \rightarrow \alpha$ transition the formation of the titanium oxides must occur. If this does not occur the α - solid solution is oversaturated by oxygen in other words the $\alpha^{/}$ phase is practically formed, for which the acicular morphology is typical. The metal microstructure when the oxygen content is 0.053% oxygen (the melt № 3) is typical for technical titanium, with the increase of the oxygen contents the crystallites of α phase gain the acicular morphology.

At the following stage the metal after heat treatment was researched. Annealing was conducted at the temperature 1100^0C with cooling in the furnace and tempering at the temperature 1100^0C with cooling in water. On the figure 3 the graph of dependencies of hardness after annealing, tempering and in the as-cast condition on the oxygen contents are given.

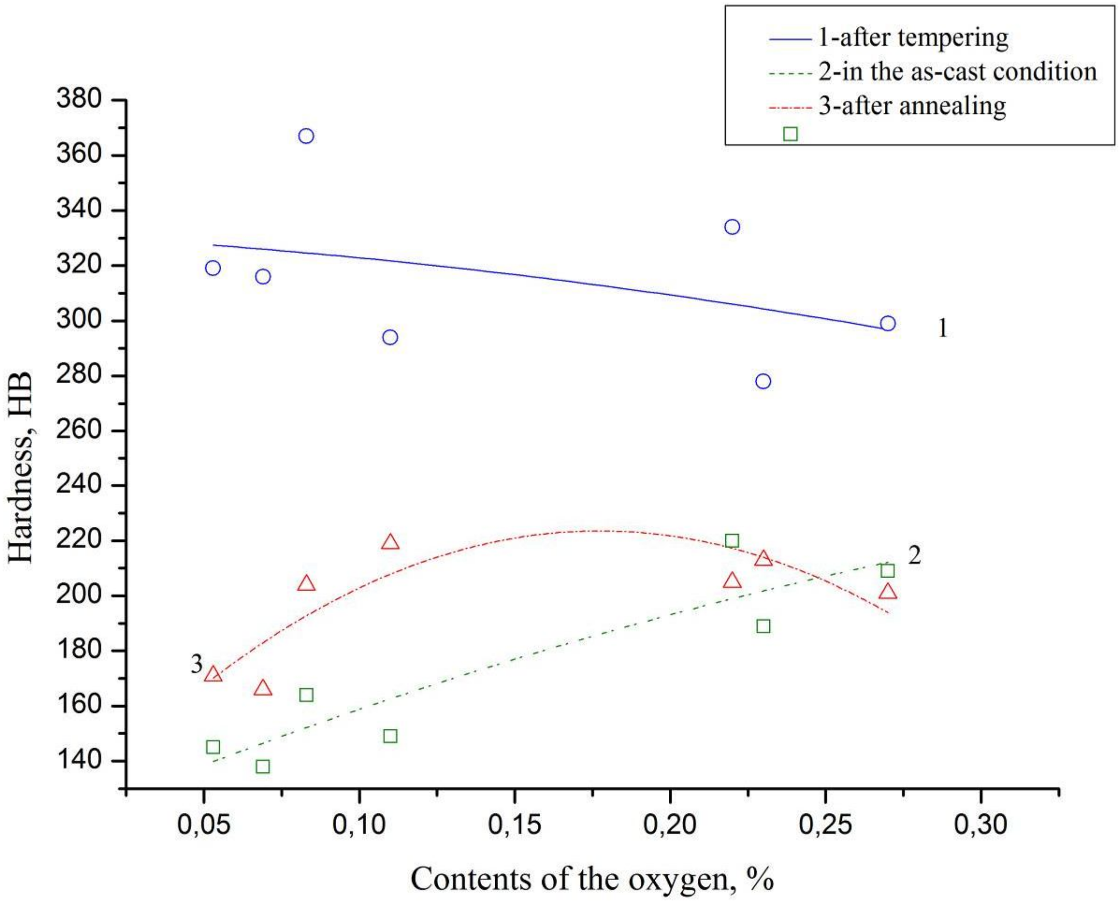
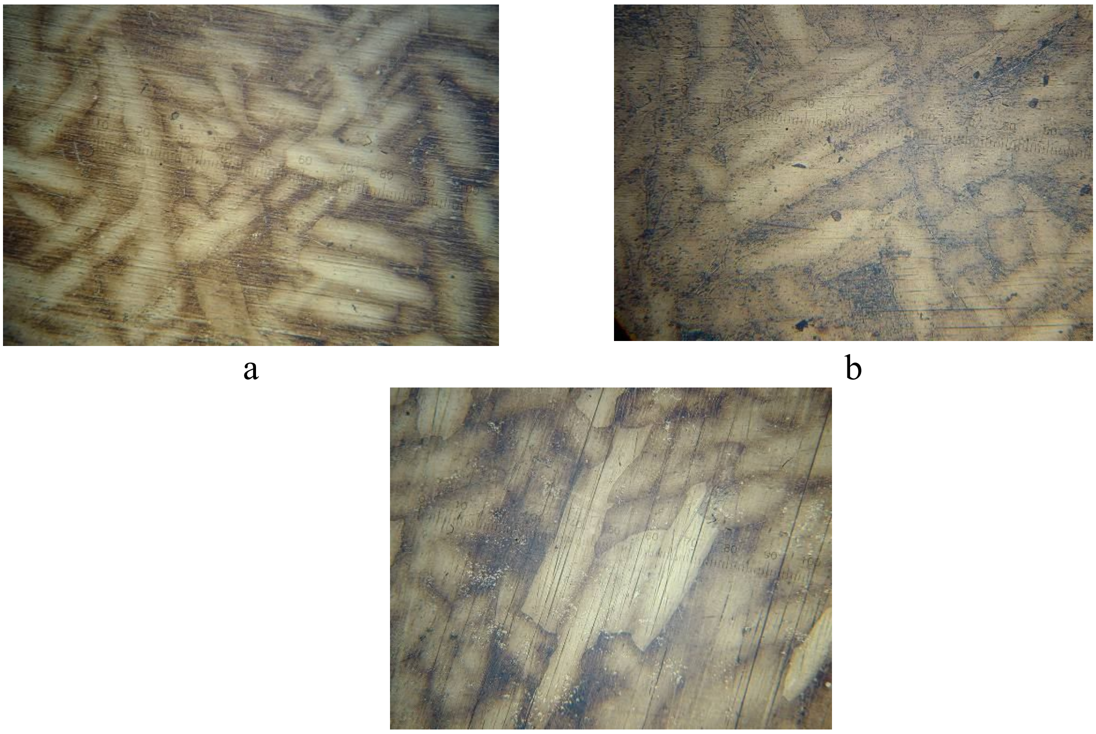


Figure 3 – Dependency of hardness after annealing, tempering and in the as-cast condition on the oxygen content

From the figure 3 it is evident that hardness of the samples in the cast state evenly increases with increase of the oxygen contents. In the annealed state hardness reaches the maximum at the oxygen contents 0.110% and after tempering hardness monotonously falls with the increase of the oxygen contents. After tempering the increase of hardness in contrast with the as-cast and annealed conditions is seen.

The structures of the samples after annealing are shown on the figure 4.

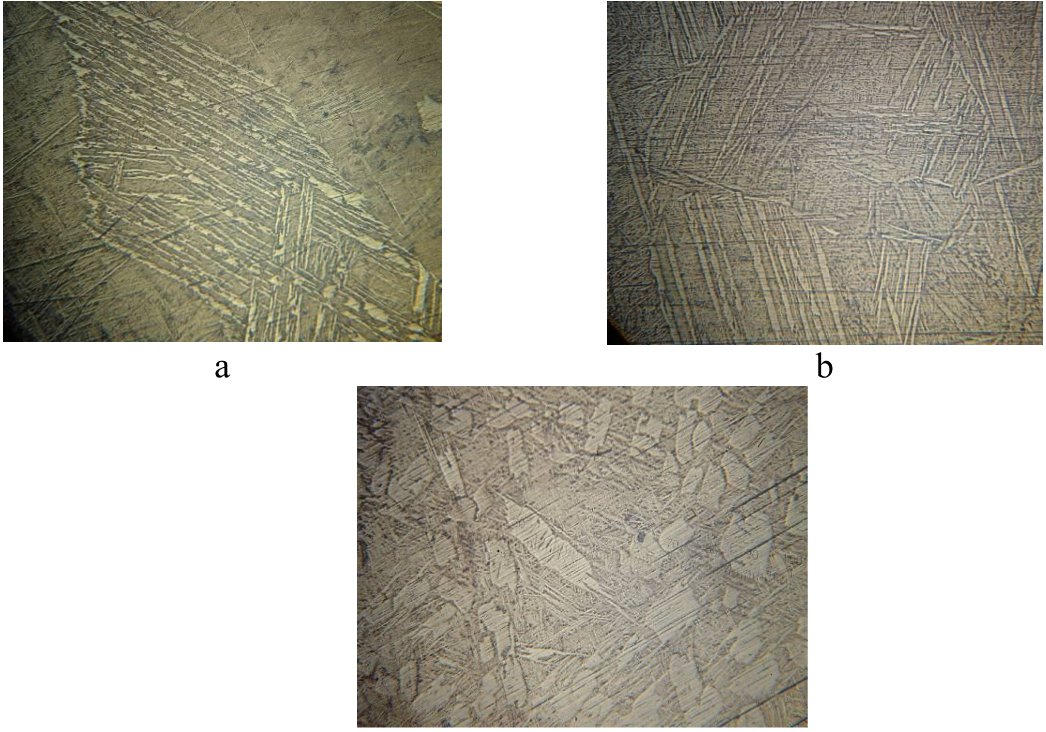


a b

c

Figure 4 – Microstructure of the metal in annealed condition, x100: a-([O]=0.053%, the melt № 3; b-([O]=0.083%, the melt № 1; c-([O]=0.230%, the melt № 7

The structure of the samples after tempering is shown on the figure 5



a b

c

Figure 5 – Microstructure of metal, x100: a-[O]=0.053%, the melt № 3; b-[O]=0.110%, the melt № 2; c-[O]=0.230%, the melt № 7

From the figure 4 and 5 it is seen that in the melt № 3 and 5 the acicular structure is observed, which is typical for the titanium alloy in the tempered condition and in the melt № 6 the comparatively equiaxial grains appear. Under the raised velocity rates of cooling and at the increase of the oxygen contents the structure in the area of α phase changed from the equiaxial on to the acicular one.

Conclusions

1. The technology ChESR allows to get the titanium ingots with the necessary contents of oxygen, changing within the range from 0.05 to 0.27% by mass to high homogeneity of its distribution in the ingot volume is observed.
2. With the increase the oxygen contents hardness of the material in the as-cast condition is monotonously increased, in the annealed - it reaches the maximum with the oxygen contents 0.110%, after tempering - monotonously falls.
3. Under the raised velocity rates of cooling the increase of the oxygen content brings about the change of morphology of the α phase area from the equiaxial to the acicular one. After annealing the influence of oxygen on crystalline morphology is not revealed.

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