THE ALLOYING OF TITANIUM BY OXYGEN IN THE PROCESS OF CHAMBER ELECTRO-SLAG REMELTING

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Abstract

The possibility of using oxygen as an alloying component in the process of chamber electroslag remelting (ChESR) of titanium sponge is considered in this work. Controlling its contents in the metal in some degree, it is possible to reach the optimum correlation between the plastic and strengthening characteristic of the titanium alloy. This is particularly important for a medical product, for which along with the mechanical properties corrosion stability and biocompatibility go to the first plan. In contrast to other alloying components (for instance, vanadium), oxygen is more safe.

For obtaining titanium, alloyed by oxygen, the chamber electroslag remelting is used. This process successfully allows both refining and alloying titanium by different elements, including oxygen, obtaining its uniform distribution on horisontal and cross sections of ingots. The process provides simultaneous melting of the consumable electrode metal, 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.
As the ligature from titanium sponge with increased content of oxygen after the special alloying in the magnesium thermic reduction process and gaseous oxygen as the argon-oxygen mixture were used. The results of research have proved that ChESR provides the increase of the oxygen contents in 2-7 times as compared to initial date (to the level 0.44 %O).

The strength properties of titanium increase with increasing the oxygen content with corresponding decreasing of plasticity. Oxygen in titanium noticeably influences the metal structure formation. So, for titanium with contents of the oxygen from 0.053 to 0.110%, a coarse dendritic structure is typical, in which differences between separate areas are revealed even under small magnifications.

Increasing the contents of oxygen up to 0.2% and above provides the formation of structure of the shear transformation, which promotes the growth of the strength properties. It is possible to explain the formation of such structures in as-cast titanium by increasing the contents of oxygen, which influences kinetics of the phase polymorphic transformation in the metal during cooling.

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

Introduction

Among the perspective construction materials, mastered in the last few years by industry, titanium and its alloys occupy the special place. The constantly broadening application of these materials in different fields of industry is explained by the favorable combination of their physical and chemical properties.
Traditionally for melting the titanium ingots the vacuum-arc, plasma-arc and lately electron beam remeltings are applied. As the whole, they meet the market demands, however, there are tasks which are difficult or impossible to be solved by traditional processes of special electrometallurgy. Among them there are: the refining of titanium from oxygen, nitrogen and, so-called nitrogen rich inclusion, as well as the alloying of titanium by oxygen and the producing of complex-alloyed materials. As the range of works, fulfilled in the Donetsk National Technical University (DonNTU) has shown, the electro-slag remelting of metals and alloys can extend possibilities of remelting processes under the active slag systems in the furnaces of a chamber type in the controlled atmosphere (ChESR) [1]. All advantages of «classic» electro-slag remelting – the refining slag environment, directed crystallization and good surface of ingot are characteristic for the chamber electro-slag remelting. The presence of the chamber in the furnace allows to conduct the remelting of high-reaction metals and alloys, including titanium, in the controlled atmosphere. In addition, metallic calcium in the slag system provides the low partial pressure of oxygen and nitrogen in the slag and gas phase, that creates the favorable conditions for the refining of titanium even from nitrogen-rich inclusion and oxygen [2-4].

The theoretical bases of this process have been developed in DonNTU, the basic laws have been investigated, technologies of manufacturing the commercial ingots from different metals and alloys, including titanium, have been created and realized [5,6].

The Alloying of Titanium by Oxygen

It is possible to consider oxygen in titanium as a perspective alloying element for the obtaining of new economically-alloyed materials. There is a considerable increase of the strength characteristics while the plastic properties fall just a bit. At the same time at the concentrations of oxygen more than 0.7 $\%_{weight}$ titanium fully loses a possibility for a plastic deformation. The compounds of oxygen with titanium are harmless for a human organism and widely used in pharmaceutics and medicine.

However, today the main problem of producing the titanium alloys, alloyed by oxygen, is connected with difficulty of obtaining the determined content of oxygen and its homogeneous distribution in an ingot. For the decision of this problem the chamber electro-slag remelting was applied as a base process. It allows to provide a high purity, and also structural and chemical homogeneity of material due to the uniform melting of the consumable electrode and simultaneous crystallization of an ingot, which flow in the conditions of chemical vacuum due to the presence of active components of flux (in particular, metallic calcium).

For the alloying of titanium by oxygen the residues of the reaction mass from the lids of retort for obtaining the titanium sponge [7], and also gaseous oxygen [8] are used as the sources of oxygen. In the case of application of the residues, the electrodes – «satellites» were produced and welded to the basic electrode, pressed from the titanium sponge of TG-110 grade (Figure 1). The obtained combined electrodes were remelted in the copper water-cooled crucible with the diameter 115 mm and heights 500 mm. According to the developed technology the set of titanium ingots is melted with the content of oxygen in the range from 0.044 to 0.40%.

In this work we considered the possibility of the alloying of titanium by oxygen directly from the gas phase in the process of chamber electro-slag remelting of titanium sponge with different initial content of oxygen. The application of the gaseous oxygen for alloying appears the most economic expedient. Out of all known, metallurgical processes of the melting of titanium the chamber electro-slag remelting (ChESR) is the most suitable for using such source of oxygen, because the alloying of titanium by oxygen from the gas phase during the process of vacuum-arc and electron beam remelting is difficult due to the presence of vacuum in the working space. The ChESR, unlike traditional ESR, allows to create in the working space any atmosphere and effectively refine and additionally alloy the metal.

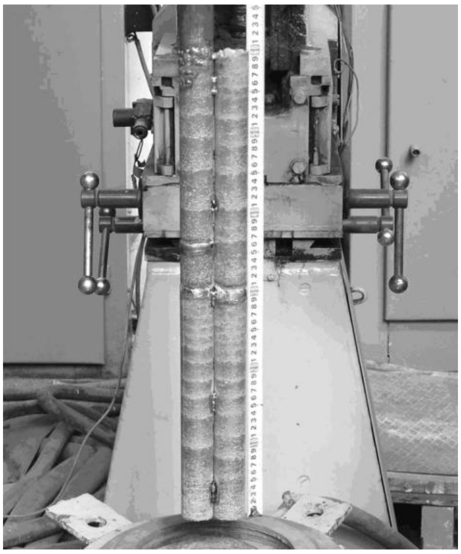


Figure 1. Pressed combined consumable electrode

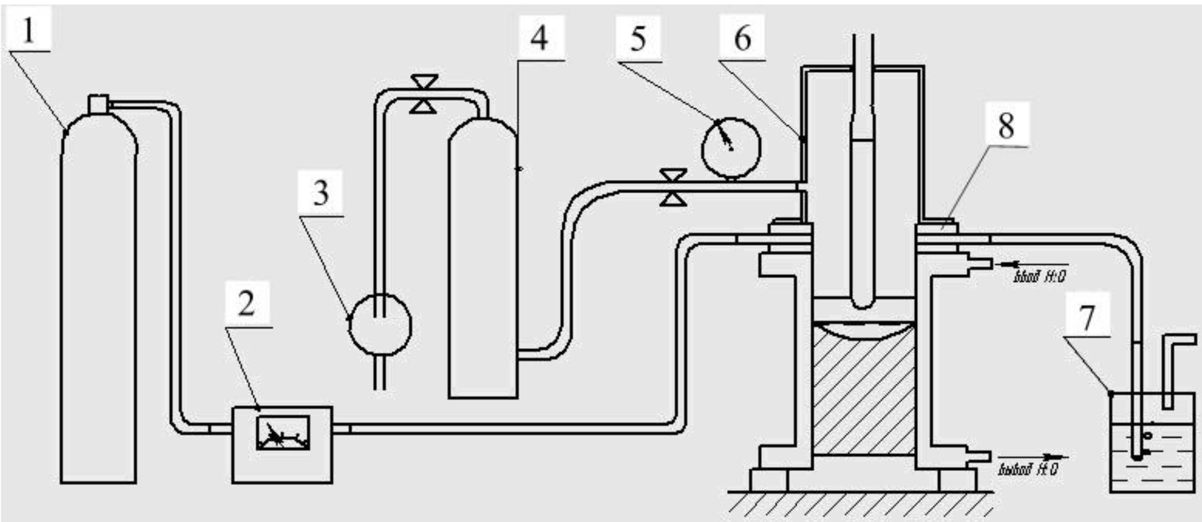


Figure 2. The scheme of the enter gases in melting chamber of ChESR:

1 – the balloon with argon-oxygen mixture; 2 – gas counter; 3 – vacuum pump; 4 – intermediate camera-filter; 5 – vacuummeter; 6 – defensive cover; 7 – water shutter; 8 – sealing laying with holes for enter the gas in the worker space.

The pressed electrodes by a diameter 40 mm and length 600 mm have been remelted in the crucible with diameter 60 mm in the chamber electro-slag furnace, developed on the base of the equipment A-550. The equipment was additionally fitted by cylinders with argon-oxygen mixture, and also devices for control the consumption and pressure of gases (Figure 2).

During the melting in the system the overpressure of gases (to 25 kPa) was supported for compensation of its possible losses. As the source of gaseous oxygen, argon containing 0.002% oxygen (GOST 10157-79) and specially prepared the argon-oxygen mixture (O_2=30%) were used. The necessary amount of argon and the argon-oxygen mixture blown in the working space of the furnace for alloying titanium by oxygen, was determined with the help of the calculation. In the calculation accepted the mass speed of remelting is equal 6.0 g/s, and consumption of oxygen is 100%. Then for the increase of the oxygen content in metal by 0.1% is necessary to introduce the argon-oxygen mixture (30% O_2) with the consumption 0.011 l/s, and technical argon – 15 l/s.

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 = 40.0 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 ingots of titanium with different content of oxygen (from 0.035 to 0.270 % O) were obtained. The experiment parameters are summarized in table 1.

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

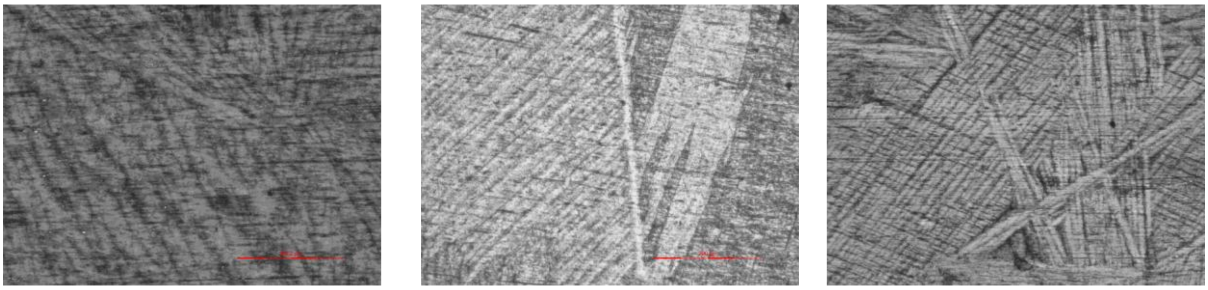
No	Electrode	Slag	Atmosphere in furnace	Content of oxygen, %
1	Titanium sponge alloyed by oxygen	CaF_2+Ca (2.5%)	Argon (the stagnant atmosphere)	0.110* / 0.083
2	Titanium sponge, TG110	CaF_2	Argon (the running atmosphere)+ mixture of Ar +O_2	0.035 / 0.110
3	Titanium sponge, TG110	CaF_2	Argon (the stagnant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

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

Influence of Oxygen on Structure and Properties of Titanium, Alloyed from Gas Phase

The structure was investigated with the help of the microscope Carl Zeiss "Axiovert 40 MAT" and "Neophot-21" with magnification of a microscopic image from 50 to 500. For the reason of studying the influence of the heat treatment on the structure and properties of the as-cast metal, the annealing at the temperature 1100^0C with cooling in a furnace and tempering from temperature 1100^0C with cooling in water were conducted.

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 converted into HB values. It was established that change of hardness along the cross section is changed with the change of the oxygen contents. Under the lowered oxygen contents, hardness is uniform on the sample cross 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 samples in the as-cast condition is given on the figure 3.



a b c

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

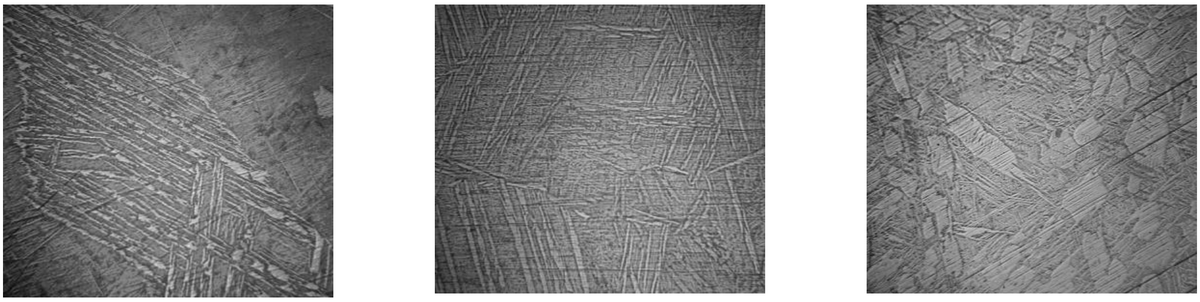
As it is seen from the figure 3 in the melts № 3, 1 and 5 the uniform single-phase structure is formed, however, its morphology depends on the oxygen content. The formation of the structure can be connected with the influence of oxygen on kinetics of the transformation. The equilibrium solubility of 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. The structures of the samples after annealing are shown on the figure 4. As it is seen the structure in all melts is globular, however with increasing of the contents of oxygen the structure becomes more coarse.

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

On the figure 5 the structures of titanium with different contents of oxygen after tempering are given. For them it is typical to have the dispersed needle-shaped structure.



a b c

Figure 5. Microstructure of metal after quenching, x100:
(a) [O]=0.053%, the melt № 3; (b) [O]=0.110%, the melt № 2; (c)[O]=0.230%, the melt № 7

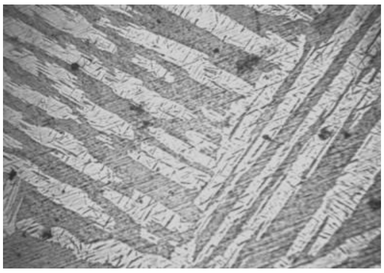
Whereas it was pronounced the suggestion about strengthening titanium under influence of oxygen as a result of forming an oversaturated solid solution and the following precipitation of dispersed particles, corresponding heat treatment was fulfilled.

As was established by metallographic investigation, the specific changes in the structure are not existent, however the needle-shaped structure reveals in a more detailed way that can be connected with increasing of etching and revealing the finer details of the structure in contrast to the tempered condition. However after this regime of the heat treatment in the structure the formation of dispersed particles was not revealled .

In this connection the following stage of the heat treatment was conducted, which consisted of heating in the furnace under 1100 ^{o}C, holding in it for 1 hour and cooling in furnace; quenching in water and ageing under T=500 ^{o}C, holding in the furnace for 4 hours. For this treatment the most characteristic samples were selected – with contents of oxygen 0.053% and 0.270%, accordingly.

As it was seen after annealing a globular structure is found, after quenching – the needle-shaped one, but after ageing the nature of etching is changed and the needle-shaped structure becomes more disperse. In addition, the samples were researched on an electronic microscope for the reason of detecting the oxides, however as we can see oxygen remains in solid solution and no oxide particles are formed.

If it is expected that oxygen is found in solid solution, so this must be revealed in changing the temperatures of the phase transformations in alloys with different concentration of oxygen. With the purpose of checking this suggestion we chose the following scheme of the heat treatment: heating at the temperature at 910 ^{o}C with the following immediate cooling in water, quenching with preliminary cooling on air for 5 sec and 20 sec. The temperature of heating is chosen so that the sample with content of oxygen 0.053% undergoes through the alpha-beta transformation, but the sample with content of the oxygen 0.270% is found in two-phase area.
As it is seen on the figure 6, in the sample with content of oxygen 0.270% the two-phase structure is found, as under this temperature according to equilibrium diagrams [9] of the titanium-oxygen system, we fall into the two-phase area. It is also interesting to note that the sample with content of oxygen 0.053% at holding on air for 5 sec with the following cooling in water, the two-phase structure also exists. This can be connected with the fact that when cooling on air we also fall into the two-phase area. In rest of the samples the single-phase structure exists.



a

b

Figure 6. The structure of the samples after the quenching from 910^{o}C:
(a) melt №7 ([O]=0.270%), direct cooling; (b) melt №3 ([O]=0.053%), cooling after 5 second pause on air

Conclusions

1. The technology ChESR allows to obtain the titanium ingots with the determined contents of oxygen, changing within the range from 0.053 to 0.270% by mass, the high homogeneity of its distribution in the ingot volume is observed.
2. With the increase of 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.
4. During slow cooling with increasing the oxygen content the size of structure components is increased but quick cooling smoothes the difference in the structure.
5. In all range of the investigated samples with different contents of oxygen, the stable substances of titanium with oxygen of the type TiO_2 are not formed, but the formed oxygen containing phases are metastable.

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