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# INTRODUCING CARBON NANOPARTICLES IN TITANIUM DURING CHAMBER ELECTROSLAG REMELTING (CHESR)

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## Abstract

The possibility of introducing carbon nanoparticles in titanium during ChESR is currently under investigation at DonNTU. Theoretical evaluation of phase and structure formation during crystallization was fulfilled by using the binary phase diagram of titanium and carbon. Within the investigations, consumable electrodes with previously introduced dispersed carbon particles were prepared by pressing of titanium sponge and nanoparticles of different types. The subsequent remelting was performed under a protective gas atmosphere in a 724 kW ChESR furnace. The average carbon content after remelting was in the range of 0.03 – 0.34 wt.-%. An increased carbon content simultaneously resulted in an increase of hardness from 140 to 220 HB. Metallographic investigations of precipitations in metal have shown phases mainly consisting of titanium-carbide particles with nonstoichiometric composition. As a result it could be stated, that structure as well as hardness show that ChESR provides good chemical and structural homogeneity of titanium ingots.

## Introduction

Among structural materials, titanium and its alloys occupy a special position. Due to its properties, titanium is considered as a basic structural material for many industries, including the aero or medical sector. In the latter case, beside high specific strength and resistance to impact loading, the most important requirements for medical titanium alloys are corrosion resistance, biocompatibility and the absence of toxic elements. The most common titanium alloy for medical applications is alloy type Ti-6Al-4V (Grade 5). However, under certain conditions the presence of vanadium in this alloy can lead to the formation of toxic compounds in the human body [1-6]. To eliminate this drawback, vanadium can be replaced by a safer alloying component, oxygen [7-13] or carbon in particular [14]. Carbon is classified as a α-stabilizer - element that increases the temperature of the polymorphic transformation of titanium. Titanium reacts with carbon, forming a narrow field of β- and α-solutions and a chemically stable compound: titanium carbide (Figure 1).

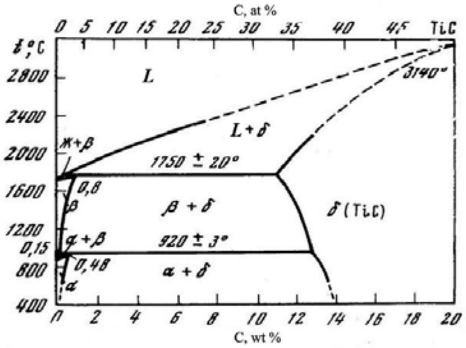


Figure 1: Phase diagram of the binary system Ti-C

The solubility of carbon in β-Ti at the peritectic temperature (1750 ºC) is ~ 5 at.-% and almost constant at low temperatures. The maximum solubility of carbon in α-Ti at 920 ºC is ~ 2 at.-% (0.48 wt.-%) and decreases as the temperature decreases from 0.48 wt.-% at 920 ºC to 0.05 wt.-% 20 ºC [15]. Therefore, when the carbon content is higher than 0.1 wt.-% the precipitation of carbides in the structure of titanium appears [16]. Carbon, like oxygen, is a good alloy strengthener. Its strengthening coefficient is 7-8 MPa per 0.01 wt.-% (Figure 2) [14-16].

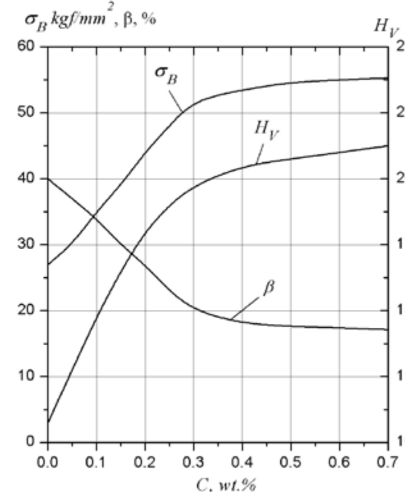


Figure 2: The effect of carbon on hardness, strength and ductility of titanium

According to Figure 2, small amounts of carbon (up to 0.35 wt.-%) can be considered as an economical alloying element that enhances the strength of titanium. With a further increase of the carbon content the plasticity of titanium decreases.

By controlling the carbon content in the metal phase in the range of 0.15-0.35 wt.-%, it is possible to reach the optimal ratio of plasticity and strength characteristics of the material. In this case it is very important to ensure a uniform distribution of carbon in the metal and the desirable form of its existence in it. This can be achieved by applying appropriate technologies for melting and the appropriate ligatures.

As carbon "ligatures" in this work micropowder of carbon and carbon nanotubes were used. The introduction of dispersed particles during crystallization of the material, or the formation of these particles in the material as a result of phase transformations during cooling is effective in means of enhancing of the structure. Even if the main structural elements (grains) are not granulated up to nano-scale, a nano-substructure can be formed in the material. This allows an increasing contribution of substructural strengthening in material properties. The introduction of nanosize particle which leads to the subsequent formation of a nano-substructure can also allow to realize the mechanisms of strengthening due to inhibition of dislocation motion, which allows to reach the increasing of strength and ductility of the alloy.

This mechanism can be realized by the introduction of carbon nanotubes in titanium. If the carbon in titanium is present in non-equilibrium concentrations, the formation of dispersed precipitates of titanium carbide during cooling phase is possible. The number and size of these particles can be controlled by changing the carbon content in the material or the heat treatment of the obtained alloy. For the practical implementation of this approach the chamber electroslag remelting (ChESR) process can be used. In addition to refining in a controlled atmosphere, this process offers the possibility of additional alloying during remelting. ChESR provides, as other remelting processes, a good structural and chemical homogeneity of the ingots with a typical as-cast structure.

## Experimental

The semi products for setting up the consumable electrodes were made by pressing of titanium sponge grade TG-110 in blocks with a diameter of 41 mm and a length of 150 - 200 mm. In the obtained blanks axially holes with the diameter of 4.0 and 6.5 mm were drilled (Figure 3), in which carbon in the form of powder (~15 µm) and nanotubes (CNT ~15 nm) were pressed. Afterwards, the blocks were welded by argon-arc welding to consumable electrodes with the already mentioned diameter of 41 mm and a length of 550-650 mm. The content of the main impurities in the initial electrode (sponge TG-110 grade) is: C = 0.03 wt.-%; O = 0.04 wt.-%; N = 0.02 wt.-%.

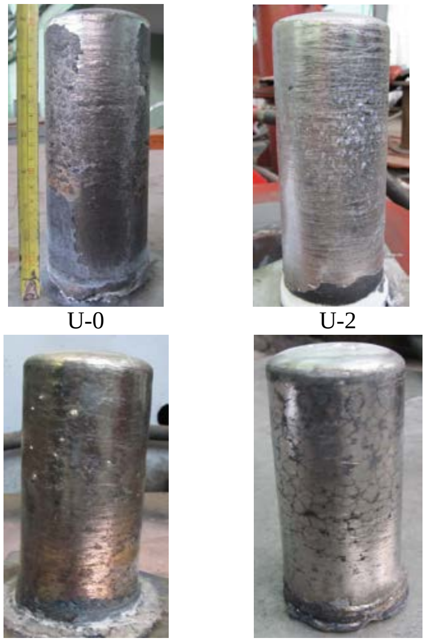
Figure 3: Pressed block of titanium sponge with carbon powder filled into the drilled axial hole

The electrodes were remelted in a chamber electroslag furnace with a maximum power generator output of 724 kW. The ChESR is based on an A-550 unit (Figure 4) with a water cooled copper crucible. The crucible possesses a diameter of 70 mm.

The refining parameters and the results of the chemical analysis are shown in Table I. It can be seen that all the considered variants of melting parameters result in an accordance of the calculated and the achieved carbon contents in the range from 0.022 to 0.34 wt.-%. This indicates the good assimilation of carbon in the ChESR process. In this case, an increase of the oxygen content and the reduction of nitrogen is about 1.5 times compared with the initial contents in the titanium sponge.

Figure 4: The chamber electroslag furnace A-550 (724 kW)

The remelting was conducted under a flux of pure $CaF_2$ (TU 6-09-5335-88). The flux was melted directly in the crucible, using the technology of "solid" start. The starting mixture was prepared of titanium chips and the operating flux. The electrical parameters of the refining maintained at U = 36.0 V and I = 2.0-2.5 kA, providing a good surface quality of the remelted ingots (Figure 5).



U-0 U-2

U-4 U-6

Figure 5: Remelted titanium ingots of the various trials: U-0-without introduction of the carbon, U-2, U-4 and U-6 with the introduction of carbon

## Metallographic studies

Samples were cut from the ingot (Figure 5) in order to conduct chemical analysis and metallographic studies. Samples for metallographic investigation of microstructure were sectioned at the ½ of ingot height level at distance ½ of radius Metallographic investigations at magnifications from ×50 to ×5000 were carried out by using optical microscopes (Axiovert 40 MAT Carl Zeiss and Neophot 2), an electron microscope (JEOL JSM-6490LV JEOL, Japan) equipped with an energy dispersive spectrometer

(INCA Penta FETx3, Oxford Instruments, England), a wave spectrometer (INCA Wave, Oxford Instruments, England) and a backscattered electron diffraction detector (HKL, Oxford Instruments, England).

Table I: Melt parameters and chemical composition of the metal

| No | Electrode material | Estimated carbon content in the ingot in wt.-% | Resulting concentration of selected elements in the ingot in wt.-% | | |
|---|---|---|---|---|---|
| | | | C | O | N |
| U-0 | Titanium sponge TG-100 | - | 0.022 | 0.067 | 0.033 |
| U-2 | Titanium sponge TG-100+CNT | 0.14 | 0.135 | 0.093 | 0.013 |
| U-3 | Titanium sponge TG-100+CNT | 0.14 | 0.13 | 0.1 | 0.021 |
| U-4 | Titanium sponge TG-100+CNT | 0.35 | 0.34 | 0.14 | 0.021 |
| U-6 | Titanium sponge TG-100+carbon | 0.35 | 0.30 | 0.11 | 0.012 |

The chemical composition of the metal was determined with an optical emission spectrometer (SPECTROMAX, SPECTRO, Germany). The gas content was determined in the laboratories of the E.O. Paton Institute of Electric Welding of the National Academy of Science of Ukraine, Zaporozhye titanium and magnesium plant and RWTH Aachen University, Germany on different analyzers (TN-114, RO-316, RH-2, RH-3, Ströhlein O/N-MAT 8500). Mechanical tests and measurements of hardness were carried out by standard methods.

The analysis of the macrostructures (Figure 6) show that the introduction of carbon in form of nanoparticles has no significant impact on the ingots macrostructure (U-2-4) and the input of carbon in form of microparticles (U-6) leads to the formation of equiaxial crystallites with reduced size.

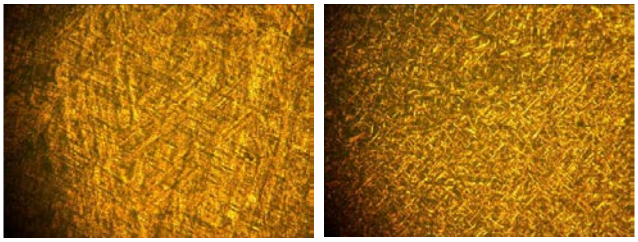
As can be seen (Figure 7, melting U-0), the structure of the metal melted without addition of carbon is typical for titanium of commercial purity and has crystallites with a large size. The carbon input of 0.135 wt.-% of carbon nanotubes leads to a dramatic structure refinement, and it changes to basket-weave morphology (Figure 7, melting U-2). With the increase of the carbon concentration to 0.340 wt.-%, the dispersion of the structure remains constant. However, the order of packets, which are typical for basket-weaving, is disrupted (Figure 7, melting U-4). When the carbon powder of micronized is used as ligature and the carbon content in the metal is 0.30 wt.-%, a structure of not oriented, approximately equiaxed, crystallites is forming (Figure 7, melting U-6). The basket-weave morphology indications are not observed.

In the present work additional investigations on the microstructure of titanium were carried out. The most typical microstructures are shown in Figure 7.

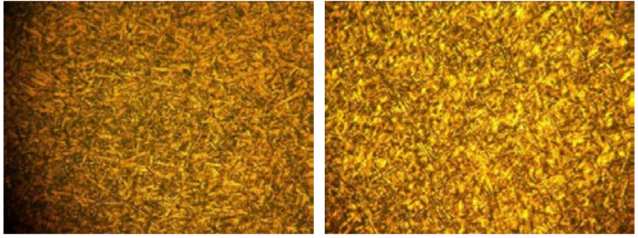
U-0, ([C]=0.022 wt.-%) U-2, ([C]=0.135 wt.-%)

U-4, ([C]=0.340 wt.-%) U-6, ([C]=0.30 wt.-%)

Figure 6: Macrostructure of the titanium ingots after ChESR



U-0, ([C]=0.022 wt.-%) U-2, ([C]=0.135 wt.-%)



U-4, ([C]=0.340 wt.-%) U-6, ([C]=0.30 wt.-%)

Figure 7: The titanium microstructure of ChESR ingots, × 100

An indirect indicator of the content and distribution of impurities in titanium is the hardness of the metal. For hardness measurement ingots were cut along the vertical axis for equal parts. Measurement was fulfilled along the central longitudinal axis of sample from bottom to top. Figure 8 shows the values of hardness, which have been measured at a height of experimental ingots.

As shown in Figure 8, the hardness of titanium correlates with its content of carbon and thus increases with its content in the metal. Thus, the maximum hardness of 200-220 HB is typical for samples with a carbon content of 0.340 wt.-% (melting U-4), and the lowest – 140-160 HB for titanium containing 0.022 wt.-% of carbon (melting U-0). Decreasing of hardness in the top of ingots may be deal with crystallization conditions in period of shrinkage elimination.

It should be noted that the different morphology of the structures of the metal melts U-4 and U-6 correlate with a difference in hardness, with approximately the same amount of carbon.

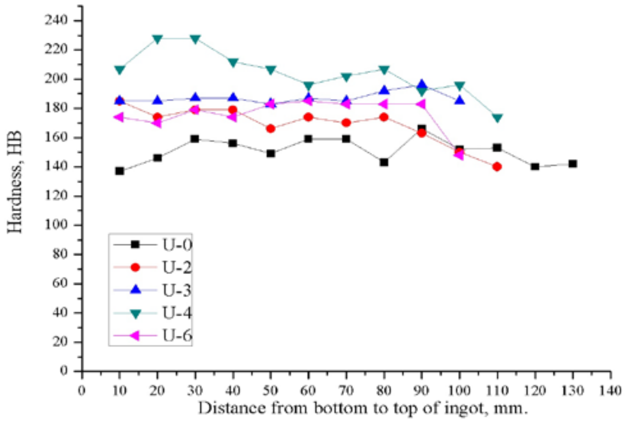


Figure 8: Measured hardness of ChESR titanium ingots

The obtained preliminary results of investigation of titanium structures alloyed with carbon and its hardness indicate the influence of carbon nanotubes on the processes of structure forming.

## Conclusions

The chamber electroslag remelting as metallurgical process illustrates an efficient way of alloying titanium with carbon in the investigated range of 0.022 to 0.34 wt.-% at the application of ligatures as carbon nanotubes or carbon powder of micronized.

The preliminary results of the investigation of the structure and hardness measurements showed that ChESR provides good chemical and structural homogeneity of titanium ingots, alloyed by carbon. In this case, there an increase of strength characteristics and changes in the structure of titanium is found.

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