THE DEVELOPMENT OF TECHNOLOGY OF HIGH-
QUALITY INGOT MANUFACTURING FROM METALS WITH 
HIGH REACTION ABILITY (Cr,Ti,V AND OTHERS) BY THE ESR 
METHOD UNDER “ACTIVE” CALCIUM-CONTAINING SLAG 
SYSTEMS.

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Over a period of more than 20 years, the development of a new variant of the Electroslag Remelting Process (ESR) has been pursued at the Department of Electrometallurgy and Converter Producing of Steel, Donetsk State Technical University (DonSTU).

The current method for producing ingots uses variations of the vacuum remelting process (vacuum-arc melting, electron beam melting). The Electroslag Remelting Process is an alternative to vacuum processes. This method is characterized by relative simplicity of equipment, flexibility of technological parameters, and high quality and low production costs of obtained metal. But “classical” ESR cannot produce ingots from such high-reactive metals as chromium, vanadium, titanium and their alloys, and it does not provide extensive refining of harmful impurities and nonmetallic inclusions.

The new direction of development for the ESR process is to use ESR in an atmosphere of noble gas under “active” calcium-containing fluxes. However, insufficient study of the theoretical and practical considerations of calcium-containing fluxes has hindered the broad application of this technology. To address this problem, investigations have been conducted at DonSTU to gain a better understanding of the technology and to demonstrate its advantages /1/.

The main goals of the investigations were to develop a theoretical basis for the technology, to study process peculiarities, and to develop and implement techniques to produce high-quality ingots from metals with high reaction ability (Cr, Ti, V and others) and their alloys with a low content of impurities.

Our theoretical investigations and calculations show that additional modernization of existing commercial ESR furnaces is necessary for practical realization of the new variant of the ESR process. To do this, a furnace operating in an atmosphere of noble gas with active metal-containing fluxes was designed and manufactured on the base of a commercial ESR unit (Fig. 1). On the basis of our experience with the new furnace, reconstructed commercial furnaces have been developed and realized in industry.
1. The manufacturing of high-quality ingots from titanium and titanium alloys

Titanium and titanium-based alloys are the important structural materials. At present they are used in the compressor sections of power generation gas turbines, turbine sections of power generation steam turbines, wing sections of aircraft air frames, compressor and fan sections of aircraft jet engines, and high-performance medical instruments and prostheses, for example. They are also used in vacuum equipment and in electrophysical devices. The Ukraine has large reserves of titanium ores (the Verkhnedneprovskoe deposit) and the infrastructure for their processing (the titanium-magnesium integrated plant in Zaporojie).

Metals with increased purity are necessary for electrophysical devices, vacuum technology and other specialized applications. These metals are currently produced by the method of iodide refining. This method makes it possible to obtain a high degree of refining from impurities.

The most widespread remelting process for producing titanium and titanium alloy ingots is the Vacuum-Arc Remelting process (VAR). The main manufacturing process for producing ingots from titanium sponge is located in Russia (VSMPO-AVISMA). This method offers the following advantages:

- high productivity
- wide range of obtained ingots size
- absence of restrictions in melting temperature of treated metal.

This is the most commonly used method for processing of magnesium-thermic titanium sponge to titanium ingot of technical purity and for alloying of titanium ingots. Despite the prevalence of the VAR technology and the broad of experience using it, material obtained with it does not meet the standards for use in physical and electrophysical equipment, units for coating deposition, vacuum units, and so on. The impurity content in most pure commercial titanium (grade VT1-00) is rather high and consists of: 0.10% (by weight) of oxygen, 0.04% of nitrogen, 0.008% of hydrogen, 0.05% of carbon, 0.20% of iron and 0.08% of silicon. A multi-stage VAR process may decrease metal quality even to the point where machining of the obtained ingot surface is required. During the melting process the carbon content in metal increases due to absorption of oil vapors from working vacuum pumps. A significant shortcoming of the VAR technology is the need for ingot surface machining (5-20 mm in depth). This machining decreases the weight of ingot up to 7-12% (average).
The essence of the technology developed at DonSTU is as follows. The consumable electrodes for ESR process from titanium sponge are manufactured by the method of pressing (Fig. 2). Consumable electrodes are subjected to the ESR process in a modernized ESR unit (Fig. 1) in an atmosphere of refined noble gas under “active” calcium-containing fluxes. The ingots of titanium are obtained as a result of remelting (Fig. 3). The impurity content is comparable to that of iodide titanium (less then 0.03% of oxygen, 0.005% of nitrogen, 0.003% of hydrogen, 0.01% of carbon).

Fig. 2 The consumable electrodes from titanium sponge for ESR

The developed technology of high-quality ingots producing from titanium and its alloys may be the alternative to vacuum remelting processes. There are large numbers of ESR units in the world that are out of operation now. After non-expensive upgrade and modernization they may be used for producing of ingots from titanium and its alloys.

Fig. 3 The general view of titanium ingots, obtained by ESR process.

One new direction for ESR under “active” fluxes is the application of the technology for refining of titanium and titanium ingots from nitrogen-rich inclusions (NRI). Work in this area is being done at the DonSTU jointly with General Electric Corporate Research and Development (GE CRD)/2/.
The particular components of interest are generally limited by low cycle fatigue (LCF). Such failures start at an initiation site and then grow by crack growth. Initiation sites for LCF failure of titanium-base alloys in the components of interest can occur at nitrogen-rich inclusions. These inclusions generally have a core of TiN, which is surrounded by a layer of $\alpha$-titanium, which in turn is surrounded by a layer of $\beta$-titanium. These inclusions are frequently referred to as “hard alpha” inclusions. In some cases the core of TiN might be absent and the $\alpha$-titanium region might be more extensive. “Hard alpha” inclusions are very brittle when compared to the surrounding alloy and are the first to crack under intense cyclic stress, thus forming an initiation site. To exacerbate the situation further, the presence of “hard alpha” inclusions frequently causes voids to form during forging or hot forming, thus increasing the size of the potential initiation site still further. The challenge, therefore, is to eliminate or minimize the size of nitrogen-rich inclusions.

Review of the phase diagram shows that all nitrogen-rich inclusions melt at higher temperatures than titanium itself. Therefore, all processes are directed toward removal by nitrogen dissolution rather than on melting.

In ESR processing of titanium alloys under “active” fluxes, the partial pressure of nitrogen in slag reaches $10^{-15}$ atm. At these conditions NRI will dissolve in slag and nitrogen will redistribute in solid solution in titanium alloy ingot. It has been established that the process of dissolution includes four stages (Fig. 4).

1. Transport of nitrogen from the nitrogen-rich inclusion to the slag, as the slag circulates past the exposed surface of the inclusion.
2. Transport of nitrogen from the slag back to the electrode face (as a dilute solution of nitrogen in the liquid metal film over the broad area of the entire face of the electrode), as the slag circulates past the balance of the electrode face.
3. Transport of nitrogen from the electrode face to the liquid titanium melt pool below, by melting of the electrode face and the forming of drops of liquid titanium containing dissolved nitrogen that fall through the slag.
4. Solidification of the melt pool to form a dilute solution of nitrogen in solid titanium. The chemical activity of nitrogen in the slag (~ 10-15 atmospheres) is maintained lower than that in the inclusion (~ 10-9 atmospheres), but higher than that at the liquid metal film/slag interface, thus maintaining a thermodynamic driving force for transport of nitrogen.

![Fig 4 Use of electroslag refining (ESR) to dissolve nitrogen-rich inclusions.](image-url)
The results obtained from our studies have shown the high effectiveness of ESR under “active” fluxes for the dissolution of NRI in titanium alloys. The rate of dissolution in this case is higher than in other metallurgical processes (VAR, for example).

1. The producing of ingots of high purity chromium.

Chromium and alloys on its base are used as alloying component for structural, tool, corrosion-, heat- and wear-resistance steels and alloys. Besides that Cr is the component of alloys with high electrical resistance and nickel-base alloys for aircraft engines parts.

With increasing of Cr purity, plasticity of it increases too. It permits to use chromium as independent structural material in the form of pure metal or alloys on its base. There are low-alloyed chromium alloys with additions of Al, Fe and rare earth metal such as VH-1, VH-2, VH-4I and other.

Chromium is used for applying of coatings by the vacuum deposition method, galvanic method, diffusion saturation method, applying by dipping and as inhibitor and so on.

In all mentioned cases the high requirements concerning concentration of impurities are applied to chromium. Content of many elements such as oxygen, carbon, aluminium is restricted at level $10^{-2} - 10^{-3}\%$ (by weight).

Existing methods of metallic chromium manufacturing permit to obtain the metal of necessary quality. There are such methods as electrolytic with following hydrogen refining (oxygen – 0.005%, nitrogen – 0.007%, aluminium – 0.006%, carbon – 0.008%, sulfur – 0.002%) and iodide (oxygen – 0.004%, nitrogen – 0.0013%, aluminium – traces, carbon – 0.002%, sulfur – 0.001%). But they have high price, low productivity and increased energy consumption. Obtained material has non-compact shape (in the form of flakes) (Fig. 5). It makes difficult using of it as structural material.

Following compacting and obtaining of cast semi-products by existing methods (VAR, for example) causes the contamination of material and decreases the quality.

In this time, the more cheap and productive methods of manufacturing of technical purity chromium exist. There are aluminotermic method (oxygen – 0.03-0.4%, nitrogen – 0.006-0.01%, aluminium – 0.1-0.5%, carbon – 0.004-0.01%, sulfur – 0.015-0.02%) and calciumhydride method (oxygen – 0.1-0.2%, nitrogen – 0.008-0.016%, aluminium – 0.006-0.03%, carbon – 0.02-0.04%, sulfur – 0.005-0.02%). Main shortcoming of this

![Fig. 5 The flakes of electrolytic chromium](image)
methods is the increased content of oxygen and non-metallic inclusions and aluminium (in aluminotermic chromium). When these methods are used, the obtained material is in the form of cast bars (Fig. 6) or in the powder form. The last one permits to produce the compact electrodes by the pressing (Fig. 7). Using of them as consumable electrodes for ESR permits to obtain the compact ingots of high-purity chromium.

It is necessary to note that in the past the ESR technology wasn’t used for pure chromium melting due to high temperature of chromium melting (1875 °C) and high vapor pressure of it. It explains the difficulties of chromium production by the another methods (vacuum remelting in particular). The technological parameters of ESR process for chromium and its alloys were developed for the first time in DonSTU.

The feature of aluminotermic chromium is the increased content of aluminium – 0.5% or more. In this connection the technology of oxidizing remelting of chromium was developed by us. Later on it was used successfully for refining of aluminotermic vanadium from aluminium.

We have developed the ESR technology of aluminotermic and calciumhydride chromium remelting and producing of alloys on its base. This technology provides the producing of quality ingots and decreasing of oxygen content from 0.5-1.0% to 0.05-0.003%, aluminium from 0.2-0.5% to 0.01-0.03%, sulfur - up to traces. Content of nonmetallic inclusions decreases in 20-25 times.

From obtained chromium ingots (Fig. 8) the cathodes (Fig. 9) for ion-plasma deposition of coatings in “Bulat” unit and targets for magnetron coating deposition were manufactured.
The pilot shipment of cathodes were tested in industrial conditions. Results of tests confirm the high technological effectiveness and increased performance of them (Fig. 10).

Developed ESR technology of high-quality ingots producing from calciumhydride semi-product was implemented in NPO “Tulachermet” (Russia).

![Fig. 8 Chromium ingot, produced by the ESR method](image1)

![Fig. 9 Cathodes for ion-plasma deposition of coatings, produced by the ESR method](image2)

![Fig. 10 The appearance of coating, deposited to ceramic base with using of targets, produced from ESR manufactured chromium.](image3)

The main advantages of developed technologies of manufacturing of high-quality ingots of titanium, chromium and alloys on their base by the ESR method under “active” calcium-containing fluxes are the relative simpleness of used equipment, high quality and low price of obtained products.