Elestroslag Remelting of Metals and Alloys under Fluxes with Active Additions in Furnaces of Chamber Type (ChESR)

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Abstract

Investigations for finding of additional refining possibilities of ESR are fulfilled in Donetsk National Technical University (DonNTU) and directed for detail investigation of refining possibilities of ESR in the controlled atmosphere in chamber furnace (ChESR) under the calcium-containing fluxes. Theoretical basis of chamber electroslag remelting, investigation of its main mechanisms, creation and realization of technology of producing of commercial ingots from different metals and alloys were developed. Physical-chemical and electrical parameters of ChESR under fluxes of $CaF_2–Ca$ system have been investigated. These works have shown the possibility of high-quality ingots production from metals with high reaction ability: chromium, titanium, rare earth elements and their alloys. In particular, the technology of high-quality titanium ingots producing with impurities concentration on the level: oxygen: 0.03-0.06 $\%_{wt}$, nitrogen: 0.005-0.006 $\%_{wt}$, hydrogen: 0.003-0.005 $\%_{wt}$, carbon: 0.01 $\%_{wt}$ by the one-step ESR in chamber furnace with consumable electrodes from pressed titanium sponge of TG-90 and TG-100 were obtained. In cooperation with General Electric (USA) the technology of titanium and alloys on its base refining from nitrogen-rich inclusions during the ESR under the calcium containing slag have been developed. It provides the inclusion refining with velocity 0.7–1.1 mm/s.

Introduction

Vacuum Induction Melting, Vacuum Arc and Electroslag Remelting processes, Electron Beam and Plasma-Arc Cold Hearth Melting are the main technological processes of metals and alloys producing for critical fields of application, aviation for example. Combination of these processes or twice-thrice repeated remelting is accepted for producing of metal with extra quality. But in many cases they can not to provide the necessary quality of metal. Most pure metals are currently produced by the method of iodide refining. This method makes it possible to obtain a high degree of refining from impurities but it is very expensive, has low productivity and final product has non-compact form.

The Electroslag Remelting (ESR) 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, titanium and their alloys, and it does not provide extensive refining of harmful impurities and nonmetallic inclusions.

Nevertheless, at recent years the new information concerning such it would seem the standard process as Electroslag Remelting (ESR) were received by Ukrainian researchers. This information is evidence of principally new possibilities of ESR as for metal and alloys refining. Investigations for finding of additional refining possibilities of ESR are fulfilled in DonNTU and directed for detail investigation of refining possibilities of ESR in the controlled atmosphere in chamber furnace under the calcium-containing fluxes. These works have shown the possibility of high-quality ingots production from metals with high reaction ability: chromium, titanium, rare earth elements and their alloys [1,2].

The investigated physical-chemical and electrical peculiarities of ChESR under fluxes of $CaF_2 - Ca$ system.

Presence of chamber and controlled atmosphere creates the favorable conditions for effective refining, modification, and alloying of metals and alloys due to using of active components (calcium, rare-earth elements and other) during the remelting process. At same time, no doubt, all of this has the influence on all complexes of physical-chemical, electrical and thermal processes of remelting. Thus, the additions of metallic component (calcium in particular) in ESR slag cause the considerable changes of electric regime of remelting. In turn, it has the influence on velocity of melting of consumable electrode, power balance of process and forming of remelted ingot.

Presence in ESR slag of metallic calcium with high vapor pressure provides the series of very essential corrections of physical nature of heat evolutions during ESR. In near-electrode zone with maximal temperature, the evaporation of calcium is probable. In result of this the usual resistive regime of melting is disturbed and arc is formed. Arc discharge "blow" the calcium vapors from the near-electrode zone to the furnace atmosphere. After condensation they are forming together with vapors and droplets of slag to the "crown" on the surface of electrode and crucible. After that the arc regime changes to resistive regime and cycles may repeats again. Evaporated from interface surface “gas-slag” and blowed from near-electrode zone calcium later partially returns in reaction zone in result of “crown” submelting. Naturally, such cyclic changes worsen the stability of electric regime and may cause the decreasing of quality of ingot surface, its macro- and microstructure. Development of these effects is clearly connected with concentration of calcium in slag and increases with its growth. Thus, when calcium content in slag reaches the concentration more than 15% wt, process fully transforms to arc regime. Therefore taking into account necessity to reach the main goal of ESR– to obtain the high-quality ingots from metals with high reaction ability, advisably to support in slag the optimal calcium concentrations, close to limiting (equilibrium).

On the basis of the thermodynamic analysis of active fluxes characteristics [3], the mathematical model of behavior of metal-containing slag system components on fluoride basis (MeF_2–Me) have been created [2]. This model permits to calculate the concentration, activity, partial pressure, velocity of evaporation of metallic component and its fluoride, limiting concentration of metallic component in melted slag system MeF_2–Me. Concentration of extrinsic elements in gas phase in dependence on temperature and pressure may be calculated too. Calculated dependence of limiting concentration of metallic calcium in slag CaF_2–Ca on temperature and pressure is shown on Fig. 1.

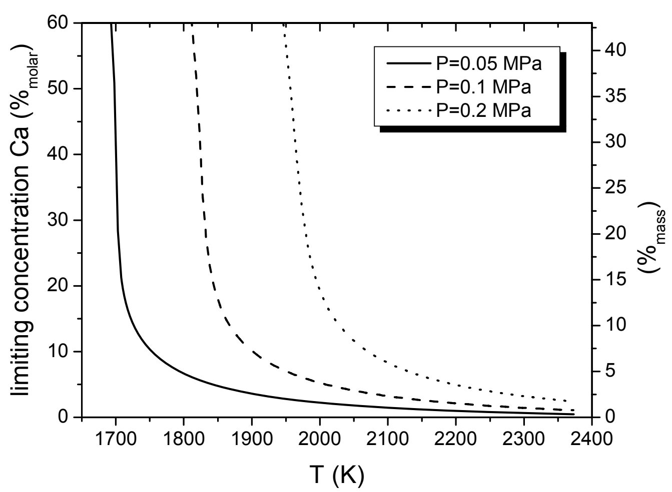


Figure 1: Calculated dependence of limiting concentration of metallic calcium in slag CaF_2–Ca on temperature and pressure

It is obvious that during the melting in these regimes it is necessary to correct the slag composition very precisely. Sampling of slag in process of melting is connected with considerable difficulties. The indirect determination of calcium concentration in slag on the basis of its concentration in furnace atmosphere doesn’t permit to obtain the high precision, because calcium content in furnace atmosphere on the different levels depends on many of complicate controlled parameters – temperature and convective flows of gas. At the same time the easy controlled parameters at ESR are the electric current and voltage. They may carry the information about number of physical parameters of electric circuit. Real electric circuits, as a rule, have in their structure the non-linear elements. In ESR unit, the slag pool has nonlinear resistance. It depends on chemical and phase state and temperature. Presence of metallic calcium in slag leads to abrupt changes in their physical properties, electric conductivity and melting temperature. It has the effect on electric characteristics of process and may cause the formation of arc discharges on the interphase boundary “electrode - slag”.

One of the methods of extracting of information from periodical signal is the spectrum analysis. Spectrum of signal is formed as the result of separation of main (carrier) signal under the action of external factors. Fourier transformations may be used to calculate the spectrum of signal:

If $x(t)$ – periodic function on t with period T, it may be represented as:

$$x(t) = \frac{a_0}{2} + \sum_{n=1}^{\infty}\left(a_n \cos 2\pi v_0 nt + b_n \sin 2\pi v_0 nt\right),$$

where frequency $v_0 = 1/T$.

Coefficients a_o, a_n, и b_n, may be calculates from formulas:

$$a_0 = \frac{2}{T}\int_{-T/2}^{T/2} x(t)\,dt,$$

$$a_n = \frac{2}{T}\int_{-T/2}^{T/2} x(t)\cos 2\pi v_0 nt\,dt,$$

$$b_n = \frac{2}{T}\int_{-T/2}^{T/2} x(t)\sin 2\pi v_0 nt\,dt.$$

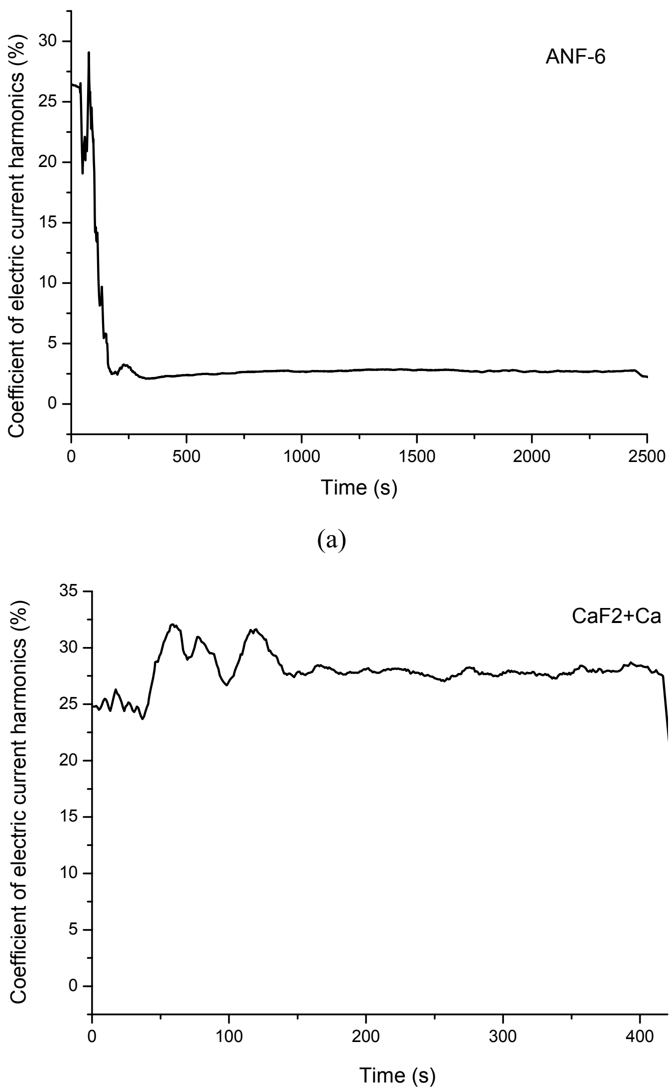
In general periodic signal contains constant component which does not depend on time and infinite set of harmonic oscillations: harmonics with frequencies $v_n = nv_0$ (n = 1, 2, 3…).

For quantitative evaluation of degree of signal nonlinearity, let’s calculate value of nonlinear distortion coefficient:

$$k_{\tilde{a}} = \frac{\sqrt{I_2^2 + I_3^2 + I_4^2 + ...}}{I_1}.$$

Analyzing and correlating the process, that take place in technological unit, with changes in spectral composition of signal, we can derive the series of dependencies. The change of current and voltage signal in dependence on metallic calcium concentration in slag may be one of them. These assumptions were examined experimentally during ESR in chamber furnace of consumable electrodes from steel 50 under different fluxes (ANF-6, ANF-1P, pure CaF_2 and system CaF_2

- *Ca*). In process of remelting the instant values of current and voltage have been recorded. After that they were processed with using of specially developed software and root-mean-square amplitudes of current and voltage, their harmonic composition and form factor have been calculated. Analysis shows that at remelting of steel under the flux ANF-6, sinusoid of current practically has not distortions and harmonics coefficient is in the range 2–3% (Fig. 2a). During remelting under the CaF_2–*Ca* system flux, the transition of ESR process to unstable arc region is possible and value of harmonics coefficient may be in the range 25–30%. (Fig. 2b) [4]. Thus, this approach may be used for on-line monitoring of metallic calcium content in slag and slag composition at real ESR process.



(a)

(b)

Figure 2: Coefficient of electric current harmonics during ChESR of steel under the flux :(a) ANF-6; (b) CaF_2*–Ca.*

The development of technology of refining and producing of various metals and alloys by ChESR.

The fulfilled theoretical investigations show that for practical realization of this process the additional modernization of existing commercial ESR furnaces is necessary. In this work much attention was devoted to development of additional equipment, which permits reequip without large investments the existing commercial ESR units in chamber furnaces for remelting in controlled atmosphere. For today the projects have been developed and reequip of laboratory and industrial-scale ESR furnaces into chamber-type ones have been fulfilled (Fig.3).

The obtained results were used for development of technology of refining and producing of various metals and alloys by ChESR. In particular, the problem of chromium ingots producing with purity close to electrolytic one from «cheap» consumable electrodes has been solved. These electrodes manufactured from material after calcium-hydride and alumothermic reduction. 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 ^{o}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 DonNTU [5]. To carry out the ESR of chromium in chamber furnace the electrodes from calcium-hydride (oxygen: 0.1-0.2 $\%_{wt}$, nitrogen: 0.008-0.016 $\%_{wt.}$, aluminum: 0.008-0.03 $\%_{wt}$) and alumothermic (oxygen: 0.03-0.4 $\%_{wt}$, nitrogen: 0.006-0.01 $\%_{wt.}$, aluminum: 0.1-0.5 $\%_{wt}$) chromium have been used. After ChESR the ingots of chromium with content of oxygen (0.003–0.02$\%_{wt}$) and aluminum: 0.005-0.03 $\%_{wt}$ were received [1,5]. From obtained chromium ingots the cathodes for ion-plasma deposition of coatings in "Bulat" unit and targets for magnetron coating deposition were manufactured [6]. The pilot shipment of cathodes was tested in industrial conditions. Results of tests confirm the high technological effectiveness and increased performance of them [6].

The technology of high-quality titanium ingots producing with impurities concentration on the level: oxygen: 0.03-0.06 $\%_{вес}$, nitrogen: 0.005-0.006 $\%_{вес}$, hydrogen: 0.003-0.005 $\%_{вес}$, carbon: 0.01 $\%_{вес}$ by the one-step ESR in chamber furnace with consumable electrodes from pressed titanium sponge of TG-90 and TG-100 were obtained [1,7]. At manufacturing of high-quality of titanium and its alloys the one of key problems is the refining of them from nitrogen-rich inclusions that present the high danger for physical-mechanical properties of material. It is known that the quality and service characteristics of parts made from titanium and alloys depend on their chemical composition, the purity of the material, and the presence of nonmetallic inclusions. So-called nitrogen-rich inclusions (NRI) are detrimental to the physical properties of this material. Nitrogen-rich inclusions have, as a rule, a core of TiNx, surrounded by layers of α Ti and β Ti, containing nitrogen. Nitrogen-rich inclusions, also known in literature as "hard alpha" inclusions, are very brittle in nature and may be responsible for cracks nucleation in metal. In this case the problem is not the general content of nitrogen in system, but the concentration of nitrogen into local inclusions that are inclined to activate cracks. Hard or brittle inclusions, pores or their combinations are often the sites for fatigue crack nucleation [8,9]. Elimination of NRI or minimization of their size has become a significant problem in the titanium industry. In cooperation with General Electric Global Research Center (USA) the technology of titanium and alloys on its base refining from nitrogen-rich inclusions during the ChESR under the calcium containing slag have been developed. It provides the inclusion refining with velocity 0.7–1.0 mm/s [10-12].

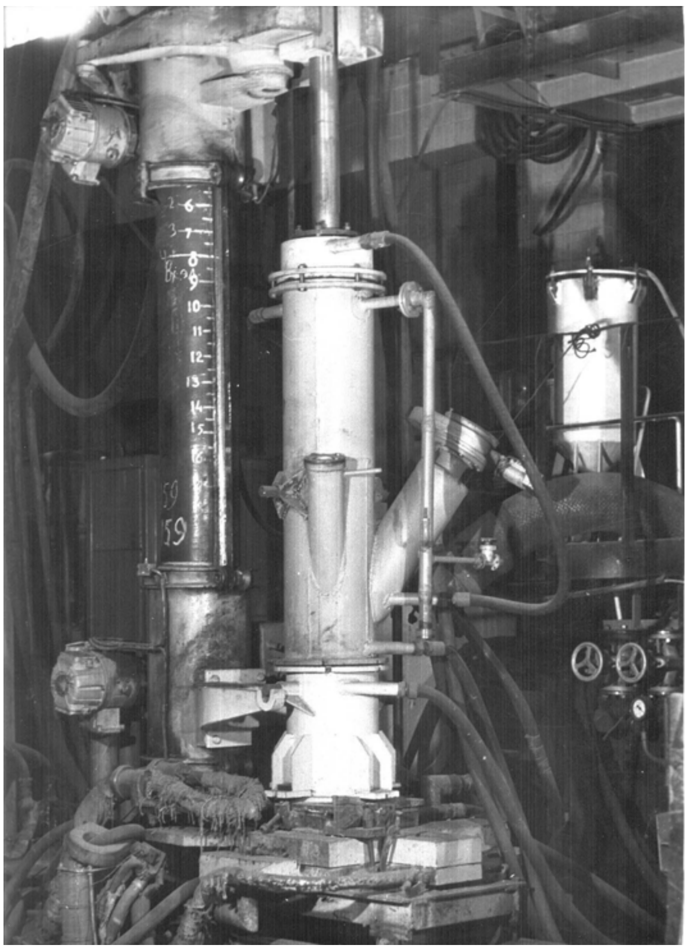


Figure 3: General view of chamber ESR furnace, manufactured on the basis of industrial unit U-578.

One of most perspective directions in the field of development of titanium alloys, with high strength and simultaneously with high thermal stability widespread in the world in last years is the development of alloys on the base of intermetallides Ti_3Al and *TiAl*. Wide application of alloys on *TiAl*-base is restrained by the absence of effective and non-expensive technologies of their manufacturing. Producing of *TiAl*-based alloys deals with difficulties, connected with differences in melting and evaporation temperatures and densities of components. Technologies of their manufacturing is very complicated and multi-stage. Methods of powder metallurgy in combination with mechanical alloying demands very prolonged grinding of components and prolonged treatment at high pressure and temperature. Development of rather simple and non-expensive methods of Ti-Al system intermetallides is very actual, but not solved problem now. Analysis of technological possibilities of ChESR process permits to make an assumption concerning possibility of its application for *Ti-Al* alloys manufacturing. Fulfilled work [13-15] confirms the principal possibility of manufacturing of ingots of intermetallic compounds on *TiAl* base by the method of electroslag remelting in chamber furnace under active flux. Obtained ingots have typical for cast material structure and increased porosity (up to 7%). Cast metal has high chemical and structure homogeneity. It is confirmed by the results of chemical, X-ray, metallographic analysis and microhardness test results.

The developed technology of high-quality ingots producing from titanium, chromium and its alloys may be the alternative to vacuum remelting processes.

The range of ChESR application may be essentially expanded in result of its using for refining and producing of steels and ferrous-based alloys. Influence of this method on structure and chemical composition of steels with different degree of alloying and carbon content was investigated. Electrodes from steels EI847B, St, 3, 50, U10, U8A, and R6M5 were subjected to remelting with varied composition of flux and furnace atmosphere [16]. Thus, during remelting of steel EI847B content of main alloying elements (Cr, Ni, Mo, Co, Nb) still practically constant. Simultaneously the effective refining of metal from sulphur, phosphorous, oxygen and nitrogen is observed (Table 1).

Table 1 Content of main impurities in steel EI847B after ChESR.

Flux , % (mass)		Atm	Content of elements, % (mass)				
CaF_2	*Ca*		*S*	*P*	*O*	*N*	*Ca*
Initial metal			0.006	0.009	0.0283	0.0770	<0.002
100	—	air	0.004	0.010	0.0058	0.0548	<0.002
97	3	argon	0.003	0.006	0.0018	0.0075	0.003
94	6	– " –	0.002	0.005	0.0040	0.0096	0.006
93	7	– " –	0.002	0.005	0.0051	0.0080	0.007
90	10	– " –	0.002	0.005	0.0046	0.0076	0.011

It was established the existence of optimum for remelting under flux that contains from 3 to 10% (by weight) of metallic calcium. Thus at 3% of *Ca* the sharp decrease of number of nonmetallic inclusions and increasing of degree of their dispersity is observed. Increasing of calcium content in flux from 7 to 10% leads to increasing of pollution of metal by nonmetallic inclusions due to appearance of calcium-containing silicates and increasing of number of crystalline nitrides (Fig. 4).

Modifying effect of calcium was evaluated over changing of primary dendrite structure. Segregation nonuniformity was evaluated by the microhardness measurement. It was established that presence of calcium in low- and medium carbon steels in small quantities (up to 0.006 %) provides the substantial modifying effect. It appears in refining of primary austenite grain size, decreasing of ferrite grain size and increasing of dispersity of peartlite. With increasing of calcium content the effect of "overmodification". It leads to formation of coarse cast structure and increasing of degree of dendrite nonunifomity.

Revealed rules are representative for ChESR of another studied grades of steel.

Application of metallic calcium in ChESR slag opens additional possibilities in alloying of metal by different elements from the slag, rare earth elements (*REE*) in particular. To evaluate them, the series of experiments have been fulfilled. Slag and furnace atmosphere composition and type of deoxidizing agent were varied in these experiments. In result have been established that ChESR in argon atmosphere under the flux CaF_2-$REEF_3$, which contains 40-80% (by weight) of *REE* fluorides permits to alloy metal of ingot up to 0.16-0.17 % of *REE*. At that degree of recovery of REE reaches 25-30 %. Introducing of metallic calcium in slag system CaF_2-$REEF_3$ in amount up to 7% increases the degree of recovery of rare-earth elements to 84.5%. Content of *REE* in metal reaches 0.54 % [17,18].

Effectiveness of direct reduction of different elements from the slag by calcium permits to use ChESR for organization of the new schemes of manufacturing of various alloys system Fe-Nd-B in particular (for example like $Fe_{14}Nd_2B$). These alloys are widely used in world practice for manufacturing of permanent magnets for medical imaging systems. Conventional technology of their production is multi-step and expensive. It is based on the separate procedures of neodymium reducing from its oxide by metallic calcium with following melting of alloy in vacuum furnace. In this work the another variant of preparing of alloy Fe-Nd-B by the remelting in controlled atmosphere of combined electrode from iron pipe with powders of neodymium dioxide (Nd_2O_3 98.7 %) and boron, pressed inside, and rod from pure iron. At that, simultaneously with melting of iron and boron, the reduction of neodymium from its oxide by metallic calcium takes place:

$$2Nd_2O_3 + 6Ca + 28\,Fe + 2B = 6CaO + 2Fe_{14}Nd_2B$$

Content of neodymium in ingot reaches 1.5-1.7 %, further increasing of its concentration in alloy may be obtained by repeated remelting of obtained ingots with additions of necessary amount of Nd_2O_3. Principal possibility of producing of alloys of Fe-Nd-B system in camber ESR furnaces at using of fluxes of CaF_2–Ca–Nd_2O_3 system have been shown in this work [19,20].

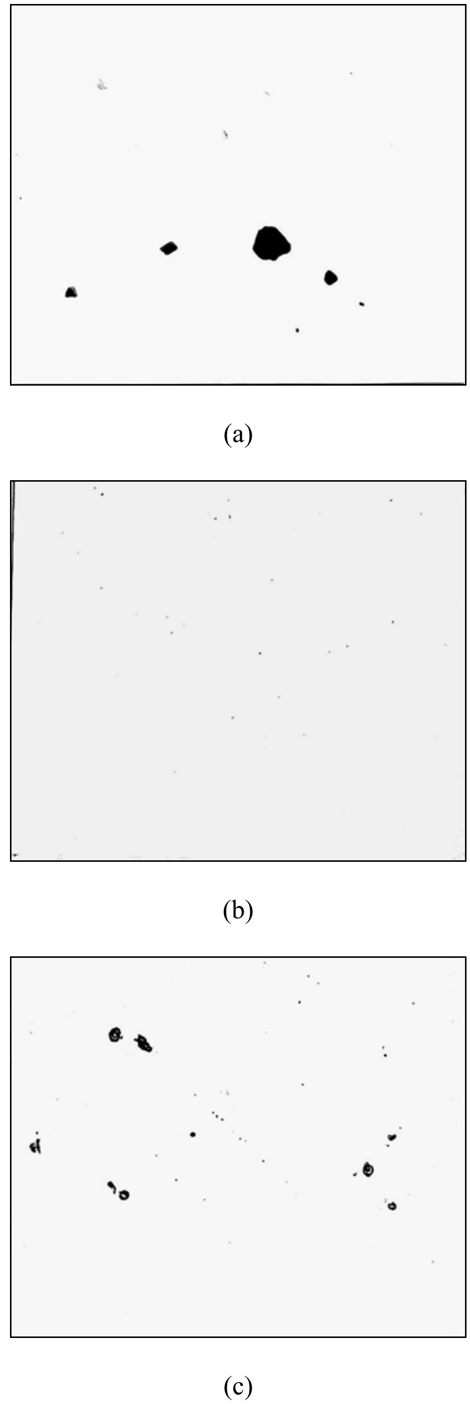


Figure4: Pollution of steel EI847 by nonmetallic inclusions ×400: (a) in initial metal; (b) and (c) after ChESR under flux 97 % CaF_2–3 % Ca and 90 % CaF_2–10 % Ca respectively

Conclusions

Fulfilled complex of investigations permits to develop the equipment and new technology of melting and refining of metals and alloys, in this number metals with high reaction ability, by the method of chamber electroslag remelting methods. Mentioned results show the perspectives of ChESR for development of the new electroslag technologies. Process is noted by relative simpleness of realization, reliability and ecological safety. In the world there is large number of ESR and VAR furnaces out of operation. After moderate revision and modernization they may be used for producing of high-quality ingots from various metals and alloys.

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