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# Use Zircon-Ilmenite Concentrate in Steelmaking

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**Abstract.** Market requirements cause a constant search for new materials and technologies, for their immediate use in increasing requirements for material and energy efficiency, as well as to the quality of steel. In practice, steel production in the tended recently of more stringent requirements for the chemical composition of the steel and its contamination by nonmetallic inclusions, gas and non-ferrous metals. The main ways of increasing of strength and performance characteristics fabricated metal products related to the profound and effective influence on the crystallizing metal structure by furnace processing of the melt with refining and modifying additives. It can be argued that the furnace processing of steel and iron chemically active metals (alkali-earth metals, rare-earth metals, and others.) is an integral part of modern production of high quality products and competitive technologies.
Important condition for development of methods secondary metallurgy of steel is the use of relatively inexpensive materials in a variety of complex alloys and blends, allowing targeted control of physical and chemical state of the molten metal and, therefore, receive steel with improved performance. In this connection the development of modifying natural materials metallurgy technologies presented complex ores containing titanium and zirconium, is a very urgent task.

## Introduction

Titanium and zirconium are strategic types of minerals and the development of their raw material base for Russia a pressing need. Russia in demand for titanium and zirconium raw are met by its own production has not more than 2–3%. Placers ore concentrates are the cheapest source of raw materials in the world are the main industrial source of titanium minerals and zircon. By the number of prospected and estimated of stocks of titanium and zirconium resources, Russia is one of the leading places in the world. However, all the known placers of Russian comparison with similar foreign fields characterized by a difficult geological and hydro geological condition for development several worse technological properties of ore sands (smaller size ore minerals, more clay content) and, as a consequence low profitability of their mastering. Therefore, when huge resources discovered placers in Russia, this resource base is not used, and titanium minerals and zircon are imported. Improving technology and increasing use of integrated ores – one of the main ways to increase investment appeal of Russian placer fields.

The major an industrial type of zirconium and titanium field are complex zircon-ilmenite placers of where is concentrated 92% and 52% of world reserves, respectively, for each component. Development this type fields plays a significant role in the economy of the various states, and especially Australia, South Africa, India, Brazil. Currently buried coastal-marine placers of zircon and ilmenite are revealed in various regions of Russia. A detailed are prospected three of placer fields, but only one of them, Tugansk (Tomsk Region), prepared for the use, the other two – Central (Tambov region) and Tulun (Irkutsk region) – are currently in need of reassessment. Previously are prospected or evaluated at the exploratory stage 7 complex zircon-ilmenite placer deposits: Georgievskoe, Tarskoe, Ordynskoe, Nikolaevskoe (Western Siberia), Lukoyanovskaya (Nizhny Novgorod region), Kirsanovsky (Tambov region), Bashpagirskoe (Stavropol Territory). At involving these facilities into operation they must be considered not only as a source of ilmenite and zircon concentrates, as well as complex fields of quartz, kaolin, titanium, zirconium, and rare earth elements.

These fields are characterized the fact that in addition to the basic element ores contain, as a rule, a large list of other metals, in the amount commensurate with the principal. In these fields of rare earth metals in the ore are elements: beryllium, gadolinium, gallium, hafnium, germanium, ytterbium, yttrium, lanthanum, lithium, niobium, rubidium, scandium, thallium, tantalum, thorium, uranium, cesium, cerium, and zirconium. All this type of ore have a large set of items, including, manganese, zinc, tin, molybdenum, lead and others. The above data give grounds be concluded that the mineral resources in Western Siberia can serve as a serious basis for the development of the metallurgical industry, the production of ferro-alloys and master alloys, stainless steel, cast iron and non-ferrous metals.

In industrial ores contains 0.5–35% $TiO_2$, in the magmatic of disseminated ore fields are usually 7–10% $TiO_2$. Placers are often characterized by low titanium content. However, relatively simple to obtain titanium concentrates from alluvial deposits make them cost effective exploitation. The mined material processed at the processing factory, where receive separate concentrates: ilmenite, rutile, zircon and others. The majority of the obtained of titanium concentrates contain an entire group of impurity elements (Sc, V, Ta, Nb, TR, Ga, and others.), representing the industrial value. Especially valuable among them is costly scandium, which is permanently contains in ilmenite (up 0.02%) and rutile (0.01%).

In Tomsk region by the Company JSC "Tugansk Mining Plant" Ilmenite "" Alexandrovsky of the South area Tugansk is mined placer fields of titanium dioxide of ore sands. Where hereinafter enrich it to yield ilmenite and zircon concentrates, chemical compositions shown in Table 1 and 2.

**Table 1**. The chemical composition of the concentrates

| Product name | Contents of components in the product, % | | | | | |
|---|---|---|---|---|---|---|
| | $TiO_2$ | $ZrO_2$ | $Fe_2O_3$ | $SiO_2$ | $Al_2O_3$ | o.i. |
| Ilmenite | 60,0 | – | – | 4,0 | 5,0 | 15,0 |
| Zircon | 4,0 | 60,0 | 1,0 | – | 1,0 | 18,0 |

**Table 2**. The distribution of the rare earth elements in the concentrate initial

| Sample | Contents of components in the product, grams per ton | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Th | La | Hf | Sc | Ce | Yb | Tb | Ta | Co |
| №1 | 446 | 1378 | 2790 | 122 | 2715 | 191 | 14,6 | 63,9 | 54,7 |
| №2 | 813 | 1335 | 2095 | 88,4 | 2054 | 142 | 30,5 | 40,6 | 25,6 |
| №3 | 649 | 1454 | 2348 | 105 | 2514 | 176 | 28,3 | 55,7 | 49,1 |

As the prevalence in the crust, titanium is ranked seventh among other elements. Titanium in the crust significantly larger than Mg, Zr, Cr, V and other elements. In the form of alloys, mainly iron, titanium is used for alloying, degassing and deoxidation of steel and alloys. In smelting of corrosion-resistant and heat-resistant steel, titanium is used as a stabilizer, linking and prevents the formation of carbides of chromium carbides. Titan intercrystallite reduces the corrosion and improves weld ability of corrosion resistant chromium-nickel steels. Steels processed containing titanium or some of it, have improved mechanical properties.

Zirconium - the only rare metal, world consumption of which hundreds of thousands of tons. More than 85% of the produced zircon feedstock used in the form of a mineral zircon containing 65–66% $ZrO_2$. Zircon concentrate (98–99% zircon) is widely used in the production of building and sanitary ceramics, refractory, and foundry services. About 10% of zircon is subjected to recycling for zirconium and its various compounds, 5% is metal and alloys. Zirconium dioxide is a valuable alloying additive in ferrous and non-ferrous metallurgy. Zirconium alloys are manufactured medical equipment and implants and thread for neurosurgery.

In industry, initial raw material for the production of zirconium is zirconium concentrates zirconium mass content of not less than 60–65% obtained an enrichment of zirconium ore. The basic methods for producing metallic zirconium concentrate – chloride, fluoride and alkaline processes.

Zirconium is an active a deoxidizer and modifier steel excelling at certain concentrations of deoxidizing aluminum capacity. Zirconium binds nitrogen in durable joints are (ZrN) and sulfur (ZrS), neutralizing their harmful impact on the quality of steel. In combination with other elements Zr increases the viscosity, strength and wears resistance of steel.

Zirconium, having a high affinity for oxygen, actively deoxidizes steel and its deoxidizing ability in conditions steelmaking processes above deoxidizing ability aluminum, whereby it prevents the formation of harmful inclusions in the steel aluminous. The formed zirconium deoxidation products easily deformed and have a thermal linear expansion coefficient similar to those of the steel, and thus during heating and cooling of the metal they do not create a tension therein, unlike aluminous inclusions that cause micro cracks. Zirconium also reduces the coefficient of oxygen activity of the melt, thereby increasing the degree of assimilation of titanium them.

Titanium and zirconium are tied into stable compounds, nitrogen and sulfur, neutralizing their harmful effect on the steel. The emerging in the steel refractory carbides, nitrides and sulfides of titanium and zirconium are used in crystallization additional center nucleation, resulting in a dense granular metal structure. When heating the treated steel with titanium and zirconium data inclusions slow grain growth, thereby preventing the occurrence of a defect such as "superheat", enabling to intensify the processes of forging, stamping, heat treatment, carburizing the metal due to heating to higher temperatures.

Lower limit of titanium content in the alloy caused by the fact that when the content of it less than 30% its expense increases and therefore silicon content in the steel. The increase in the titanium content in the alloy is more than 50% is impractical because it would result to an increase in value due to deterioration of technical and economic parameters of the alloy production.

When the content of zirconium in the alloy is less than 1% of its effects on the treated metal is weakly expressed. Zr content is more than 25% is inexpedient due to increased melting temperature of the alloy and, as a consequence, decreases in the degree of its assimilation melt.

Silicium forms stable compounds with titanium and zirconium, thus reducing the carbon content in the alloy. If silicon content in the alloy is less than 15% increases the solubility of carbon in it. Increasing the silicon content of more than 30% reduction is inexpedient consequence the content of total titanium and zirconiums in the alloy is and increase of its consumption when processing of steel.

## Formulation of the problem

One of the urgent problems of metallurgical production is to improve quality of smelted metal at relatively high cost. The need to increase the yield of metal from the smelting and, most importantly, to improve the mechanical properties of the lower cost. For example, an increase in product life of responsible assignment, in most cases, connected with decision of the metal the uniformity increasing problems in both structure and composition, and to reduce pollution steel harmful impurities. Complex alloying is not always provides the desired properties, however, researchers are trying to improve the quality of existing steel brands exposure to crystallizing or recrystallizing the metal during heat treatment and deformation. In all cases the quality and the deformed thermally treated steel depends on the structure and properties of the metal.

One of the most effective methods to improving the quality of steel is to use different methods of modification. Under the modifying understand such effects, in which considerably are modified the structure and properties at practically unchanged number of major components. Modifying of is carried by small additives soluble and insoluble impurities, vacuuming and refining, exposure to ultrasonic and low-frequency vibrations, external fields (electric, magnetic), regulation of the heat sink rate and others.

Most cost effective way to improve the quality of the steel melt modification should be considered as soluble and insoluble additives because it does not require any additional expensive equipment. Introduced into the melt small additions of soluble and insoluble impurities affect crystallization parameters dislocation structure, degassing, nonmetallic inclusions and formation of secondary phases, liquation, change of shrinkage, peel speed deformation and ingot solidification, as well as recrystallization and grain growth. Recently, been great improvements in the use of modifiers to improve the quality of steels and alloys.

Are currently a large number of modifiers mechanisms of action of hypotheses. However, most of them are not sufficiently backed up by experimental data, and those that are based on a comprehensive and in-depth research, apply only to the pure metals and binary and ternary alloys. In relation to the multi-component alloy, smelted in a production environment, this hypothesis is not entirely are valid, because it does not take into account a number of side factors, associated with the steelmaking process, but have a significant impact on the final properties of metals

To address question of the advisability modification the steel or other modifier or a mixture of the components necessary to know some of the characteristics of the melt and especially the work of formation of nuclei of gas bubbles and crystallization centers. The work formation of crystal nuclei determines the propensity to steel super cooled, which is determined by the composition and degree of purity crystallizing steel. However, the choice of fuses and modifiers associated with their melting kinetics, solubility and activity in the investigated steel.

Modifying of steel of natural concentrates or in minerals have recently has attracted considerable interest in the metallurgical steel as a source of modification. Recently, in a world practice of steel production trend replacement of ordinary carbon steels to economical high strength micro alloyed steel. For alloying of which use rare and expensive alloying elements such as vanadium, titanium, niobium, rare earth metals, barium, strontium, and others. However significant costs of the use of clean alloy elements or their alloys restrain the development directions of micro-alloying and modification of steels and alloys. Current solutions this problem is the use of natural mineral concentrates as the replacement of expensive pure elements as modifiers for micro-alloying steel. Such mineral concentrates are an excellent substitute for expensive alloying elements with micro alloying steel and more available for use.

Research on the influence different types of modifiers with varying degrees of perfection of structure and composition are of considerable interest when discussing modifying the mechanism activated or become isomorphic insoluble impurities. Of even greater interest is the work on the influence particle size and distribution of the insoluble impurities on the mechanical properties of the composite alloys, but such data are still very scarce.

## Results and Discussion

Placers are often characterized by low contents of the basic element (Ti, Zr, etc.). However, the relatively simple production of concentrates from placers makes them cost-effective exploitation. The mined material is processed at the processing factory, where receive separate concentrates: ilmenite, rutile, and zircon. Which later goes to the consumer to the corresponding production.

As a result of a series of studies on the influence of Tugansk field concentrates on the changes in the structure and properties of the steel been received results showing the characteristics of the data changes.

Steel produced by modifying existing technology using ultra disperse powders of zirconium oxide, titanium, niobium, hafnium, vanadium, aluminum, obtained from natural field Tugansk concentrate. Modifying mixture loaded onto the bottom of a pouring ladle counting 3 kg modifier per ton of steel. After holding of melting in the furnace make steel casting ladle with a modifier. After three minutes of exposure in a ladle with a modifier steel began bottling.

Influence of modifier on the quality and structural characteristics of the samples evaluated for austenite grain size, quantity, shape and distribution of nonmetallic inclusions in the grain boundaries and inside the grains, the presence of carbides.

Microsections for the study of nonmetallic inclusions were made of halves of the samples after the tensile tests, impact strength and crack resistance.

Before the metallographic analysis samples were several stages preparation of micro sections that is selected in accordance with characteristics of the sample material. Preparation of micro sections steps include:

1. Tenderloin samples cutting machine BUEHLER Delta Abrasimet Cutter using abrasive wheel HH type of metal materials and steel hardness 50–60 HRC at a constant water cooling;
2. Hot Mounting Presses in the phenol resin in BUEHLER SimpliMet 1000 automatic press;
3. The grinding and polishing machine to BUEHLER Phoenix 4000 using the following consumables: grinding of papers Buehler CarbiMet 180 grit, Buehler CarbiMet 240 grit, Buehler CarbiMet 600 grit; polishing with diamond paste tissue Metadi particle size 6 microns and 3 microns and suspension MasterPrep 0.05 microns.

Analysis of the microstructure of the metal was carried out using motorized optical microscope Zeiss Axiovert 200 MAT and Nikon Epiphot TME, which are an integral part of the complex analytical Thixomet.Pro.

Analysis of contamination of steel non-metallic inclusions carried out on thin sections not etched by ASTM E1245-03 standard and in accordance with National State Standard 1778-70 using appropriate Thixomet.Pro image analyzer modules.

In assessing the non-metallic inclusions in accordance with National State Standard 1778-70 used automated method, in which separation of oxides on the "non-deformable silicates" after recognition by the color inclusions made, "point oxides", "oxide stringers", "silicate fragile" and "plastic silicates." Assigning points conducted by the measured volume fraction for each type of inclusions on the basis of the known calibration curve "point-volume fraction."

The results of monitoring the content of nonmetallic inclusions in the metal of the samples are presented in Table 3.

**Table 3.** Results of control the content of nonmetallic inclusions in sample

| № samples | The types of non-metallic inclusions | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | OS | OP | SC | SD | CH | C | HC | HT |
| 1 | – | 0.0 | 2.0 | 2.0 | 0.5 | 2.0 | – | 1.0 |
| 2 | 0.5 | 0.0 | 0.0 | 0.0 | 4.0 | 0.5 | – | 1.0 |
| 3 | – | 0.0 | 3.0 | 0.5 | 0.0 | 3.0 | 0.0 | 1.0 |
| 4 | – | 0.0 | 1.0 | 2.5 | 3.0 | 2.5 | – | 1.0 |
| 5 | – | 0.0 | 1.5 | 0.0 | 3.0 | 1.5 | – | 2.5 |

As can be seen from the data, average content nonmetallic inclusions in the samples ranged up to 3 points. The main types of inclusions – non-deformable and brittle silicates and nitrides stitch.

Micro x-ray spectroscopic studies of the chemical composition of nonmetallic inclusions were performed on a scanning electron microscopic ZEISS SUPRA 55 VP.

Type inclusions specific encountered in the samples is shown in Figure 1.

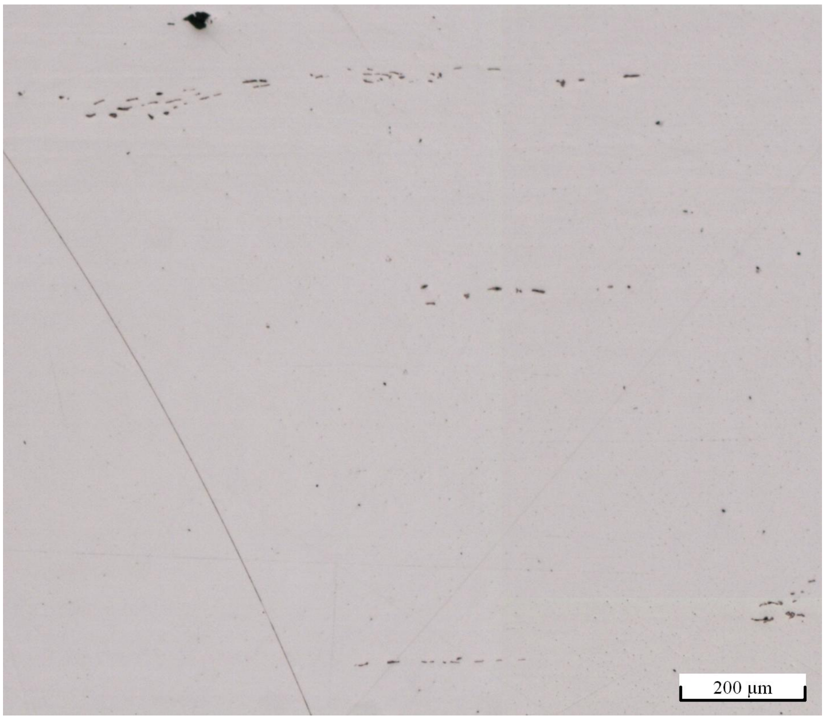


**Figure 1.** Type specific nonmetallic inclusions encountered in the sample

Detailed study of nonmetallic inclusions in the fracture detected samples for mechanical tests were conducted on selected samples in which unsatisfactory results in terms of metal plastic properties were obtained. As a result of research, it was found that the reason for the decline of properties blanks is large concentrations of nonmetallic inclusions onto the surface of the fracture. Type sample fracture is shown in Figure 2.


**Figure 2.** Type of fracture of the sample with lower plastic properties

At of metallographic research on microsections inclusion of both types were in the form of lines. To determine the composition of inclusions was their microprobe analysis was conducted, which resulted in the maps of the distribution of chemical elements contained in the inclusions.

The data obtained show that in the absence of titanium a metal are formed in the inclusions containing large amounts of calcium aluminates, and calcium and manganese sulphides. A characteristic feature of such inclusions is that they are in the form of clusters and layers on the primary grain boundary and lead to a decrease of material properties, primarily plastic. The excess of titanium contrary, leads to the formation of a metal nitride and carbonitride inclusions, which are located in the metal in the form of clusters and chains extended along the direction of deformation.

The characteristic form of the sample metal microstructure is shown in Figure 3.

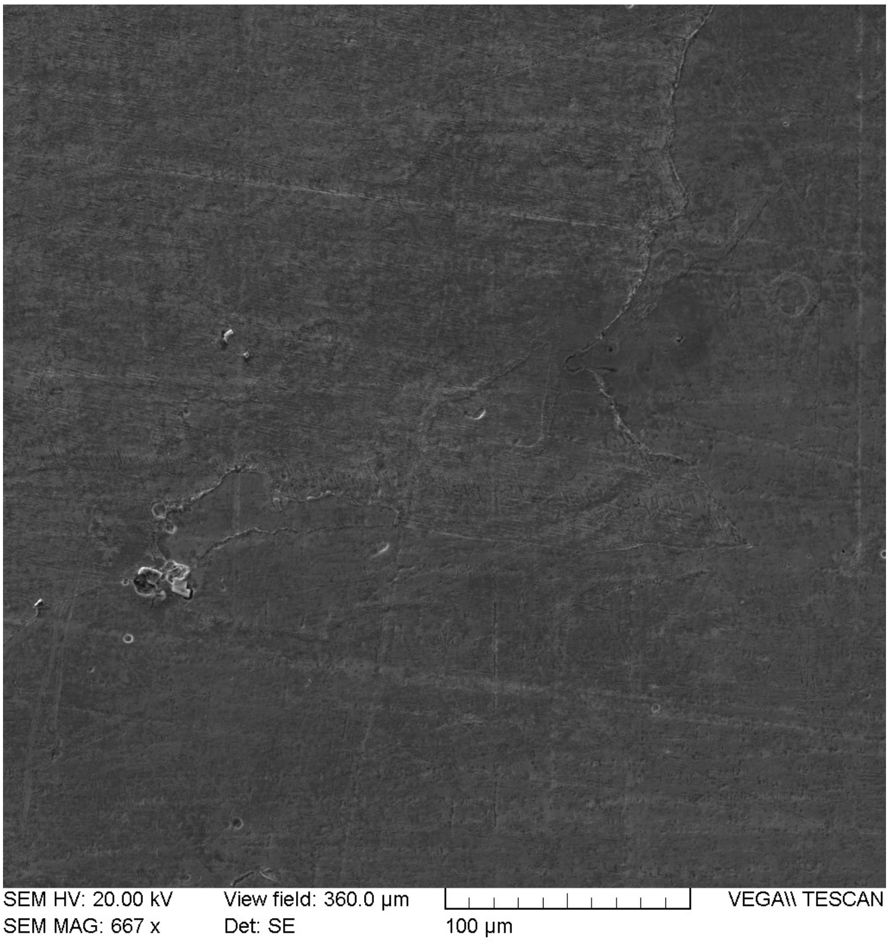


**Figure 3.** The characteristic form of the metal microstructure

As can be seen from the data presented, the metal microstructure is austenite. The size of the metal grains of both pieces is within the limits set by the requirements of the Terms of Reference.

According to the study it was found that in the macrostructure of metal and fracture free from defects: friability, bubbles, cracks, foreign objects, captivity, shells, flakes, breaks.

The study revealed microstructure of the steel sample the influence of modifier on the microstructure of the samples compared to melting, obtained by the existing technology, namely: In particular, the steel melt modification significantly improved the uniformity of steel structures, which in its turn contributes to its density and it leads to improved isotropy, i.e. enhances of uniformity of internal stress distribution under load, reduce cracking, chipping and pore formation.

The modified samples no carbides, blowholes, a decrease in the number and size of nonmetallic inclusions on the boundaries and within the grains, as well as visually observed a decrease in grain size.

## Conclusion

In the process of modifying steel zircon-ilmenite concentrate was obtained by a slight increase in the mechanical characteristics. The modification leads to reduction degree of contamination of the metal non-metallic inclusions, the fact of the presence of titanium and zirconium contributed to this.

Thus, the use of mineral concentrates perhaps steel a modifier and partial or complete replacement of expensive alloying elements. However, there is more to understand many factors influencing the properties and structure of the steel obtained in the modification.

Works on studying the influence of different types of modifiers with varying degrees of perfection of structure and composition are of considerable interest in the discussion of modifying the mechanism by activated or steel isomorphic insoluble impurities. Also greater interest working on the effect of particle size and distribution the insoluble impurities on the mechanical properties of the composite alloys, but such data is still very scarce.

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