Evaluation of the Use of Complex Mineral Concentrate as a Modifier Steel

R A Gizatulin, S N Fedoseev, R S Dariev
Yurga Institute of Technology, National Research Tomsk Polytechnic University affiliate
Kemerovo region, Yurga, Leningradskaya str. 26, RUS

e-mail: sfedoseev@tpu.ru

Abstract. Increasing customer demands for quality of the resulting metal, and in the first place, the impurities, metallurgists dictate need to develop new and improved technologies. Thus, a significant reduction in metal losses can be achieved by developing new complex alloy steels, special purpose, improving technology of their production and developing new technology of smelting to improve the physical, mechanical, foundry and operational characteristics by influencing the structure of the steel by modifying the liquid melt, change more favorable morphology of nonmetallic inclusions. For complex-alloyed steels expensive and scarce alloying elements Ti, Nb, Zr, etc., are used, which are inaccessible to conventional structural steels. In this regard, the paper also presents the results of applying of innovative modifiers containing alloying elements (Ti, Nb, Zr, etc.) based on mineral concentrates in the Tomsk region.

1. Introduction
Contemporary mechanical engineering requires the use of materials having not only improved strength, but also a series of special properties that provide a long and reliable performance parts in a variety of operating conditions. Thus one and the same steel alloying element imparts simultaneously some special properties. These are determined primarily chemical composition. Requirements for quality, performance and service characteristics of steel require continuous improvement of their composition and production technology. It depends on the increase in the life of modern equipment and machinery. In this context, an important issue is to increase the wear resistance, corrosion resistance, heat resistance, sealing et al., Which is relevant to many industries (mining, metallurgy, machine building, construction, etc.).

Resolve this issue is possible by means micro-alloying steel small additions of soluble and insoluble impurities, vacuuming and refining, exposure to ultrasound and low-frequency vibrations, external fields (electric, magnetic), speed control and other heat removal.

Most cost effective way to improve the quality of the steel melt should be considered modifying soluble and insoluble additives because is not required any additional expensive equipment. Added to the melt small additives of soluble and insoluble impurities influence the crystallization parameters, dislocation structure, degassing, formation of nonmetallic inclusions and secondary phases, liquation, change of shrinkage, deformation and solidification rate strand shell, as well as recrystallization and grain growth.

A feature of the complex modification of steel alloys is that in parallel with the changes nature of the refinement of the structure and the shape of of nonmetallic inclusions is reduced to 1.5-2.0 times the pollution of the austenite grain boundaries of the oxide, sulfide, and nitride inclusions, increased uniformity of structural components for enhanced ductility and the toughness of the steel.

But the high cost used in the modification of the alloying elements and their deficiency reduces the spread of method for improving steel. This problem can be solved by using the modification steels of...
natural mineral concentrates affluent necessary alloying elements (Ti, Nb, Zr, and others.). In this paper the use of complex mineral concentrates fields of Tomsk region.

2. Experimental methods
A study was carried out over the length of the metal and the volume of blanks and included the following tests and studies:

- Tensile testing;
- Impact test at a temperature of +20 °C – 50 °C;
- Determination of crack resistance and impact toughness on samples with a crack at a temperature of –50 °C;
- Control of macrostructure and fracture of metal;
- Control of the content of gases (oxygen and nitrogen) in the metal;
- Study of the nature and control of the content of nonmetallic inclusions;
- Study of the microstructure of metal;
- Control of the grain size and distribution.

All testing and research (including sample preparation) carried by standardized procedures, which ensures the objectivity and comparability of results, including the ability to compare the results of the previously conducted research and testing, including tests of serial production.

Control of macrostructure and bend metal, and tensile testing and impact strength at a temperature of +20 °C – 50 °C, carried directly on the manufacturer; testing and fracture toughness of the on samples with a crack at a temperature of –50 °C and a durability of metal research conducted under conditions of Nano-Center” TPU, Tomsk on samples prepared by enterprises-producers of blanks after finishing their required by the specialists of "Novosibirsk Switch Plant".

Tensile tests were conducted in accordance the requirements of National State Standard 1497-84 samples of type III № 4 \( l_0 = 5 \) \( d_0 \) latching of the following indicators:

- proportional limit \( \sigma_p \);
- yield strength \( \sigma_{0.2} \);
- the ultimate tensile stress (tensile strength), \( R_m \);
- elongation \( \delta \);
- Reduction \( \psi \).

Control was carried out on metal macrostructure Macro section prepared in accordance the requirements of National State Standard 10243-75. Etching micro sections was performed in 50% solution of hydrochloric acid at a temperature of 60 °C for 10-15 minutes.

Fractures were produced from the same plate, which was held control of the macrostructure of the metal. To do so to plates plotted incision Macro section the opposite side, and then conducted its destruction on copra or press.

Kind of macrostructures and fractures was fixed with the help of photography.

Evaluation macrostructures and fractures metal was carried out in accordance with the requirements of National State Standard 5192-78.

Control the content of gases (oxygen and nitrogen) in the metal was carried out using an automated a gas analyzer Eltra ON900.

The principle of operation of the a gas analyzer is in a molten sample of known mass in a stream of neutral gas, which captures and transports oxygen and nitrogen released from the molten metal to the spectral detector. The detector registers the integral content of oxygen and nitrogen in the transmitted stream and calculates the weight and content of the gases in the metal micro sample.

To improve the accuracy of the determination of gases gas analysis procedure conducted repeatedly for each sample and the results were subjected to statistical analysis.

Micro sections to study of nonmetallic inclusions were made of halves of the samples after tensile testing, toughness and crack resistance.

Before the metallographic studies samples passed several stages polishing, which are selected according with the features of the material samples. Stages of polishing included:

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

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

Analysis of the contamination steel non-metallic inclusions was carried out in sections of the standard ASTM E1245-03 and according to National State Standard 1778-70 with appropriate image analyzer modules Thixomet.Pro.

Micro x-ray spectroscopic studies of the chemical composition of non-metallic inclusions were performed on a scanning electron microscopic ZEISS SUPRA 55 VP. The microscope is equipped with a computer control of a system an electron beam scanning and digital recording signals and images, X-ray microanalyses INCA WAVE and INCA X-MAX.

In order to identify the grain structure of micro sections etching performed after determining the composition and the content of nonmetallic inclusions 4% alcoholic solution of nitric acid and of Marshall's reagent, consisting of two parts which are mixed in a ratio of A: B = 1:1 just before use:

- Part A: 5 ml of concentrated \( \text{H}_2\text{SO}_4 \), 8 grams of oxalic acid and 100 mL \( \text{H}_2\text{O} \);
- Part B: 30% solution of hydrogen peroxide \( \text{H}_2\text{O}_2 \).

Metallographic studies were carried out with the help of a motorized light microscope Axiovert 200 MAT at magnifications from 50 to 1000, which is part of the complex analytical Thixomet Pro.

The procedure for conducting the analysis is to build a panoramic image etched structure with an increase 1000-fold and the quantitative analysis of metal structure by intersecting concentric circles, in accordance with National State Standard 5639-82 and the appointment of grain size, by comparison with the standard scales in accordance with National State Standard 8233-56 (scale 3) in the corresponding module Thixomet.Pro an image analyzer.

3. Results and Discussion

The test results blanks volume acceptance tests after thermal treatment in various models are shown in Table 1. The test results of periodic blanks №№ R6942A2 and R6986A1, previous final thermal treatment for two different modes, are presented in Table 2.

In order to achieve sustained and higher levels of mechanical properties, especially on indicators of percentage reduction and impact toughness at subzero temperatures, additional studies were conducted and testing of modes quenching and tempering.

| Mode of heat treatment | №     | \( \sigma_p \), MPa | \( \sigma_{0.2} \), MPa | \( \sigma_t \), MPa | \( \delta \), % | \( \psi \), % | KCU\(^{+20^\circ\text{C}} \), MJ/m\(^2\) | KCU\(^{-50^\circ\text{C}} \), MJ/m\(^2\) | KCT \( -50^\circ\text{C} \), MJ/m\(^2\) | K1C \( -50^\circ\text{C} \), H/mm\(^3\) |
|-----------------------|-------|---------------------|----------------------|------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| blank № R6790A1-1    | K     | 1167               | 1324                 | 1442             | 8.0            | 37.0            | 0.33            | 0.27            | 0.10            | 2099           |
|                       | D     | 1197               | 1324                 | 1452             | 8.6            | 30.0            | 0.29            | 0.22            | 0.10            | 2276           |
| blank № R6942A2-1    | K     | 1187               | 1305                 | 1432             | 13.0           | 38.0            | 0.30            | 0.20            | 0.10            | 2001           |
|                       | D     | 1187               | 1315                 | 1462             | 8.4            | 32.0            | 0.33            | 0.24            | 0.11            | 2551           |
| blank № R6986A1-1    | K     | 1216               | 1344                 | 1481             | 11.5           | 35.0            | 0.29            | 0.20            | 0.12            | 2815           |
|                       | D     | 1197               | 1344                 | 1472             | 9.6            | 33.0            | 0.29            | 0.20            | 0.10            | 2443           |
| blank № R6986A1-1    | K     | 1167               | 1285                 | 1403             | 10.0           | 28.0            | 0.25            | 0.20            | 0.11            | 2443           |
|                       | D     | 1177               | 1295                 | 1432             | 8.6            | 31.0            | 0.27            | 0.22            | 0.11            | 2521           |
| blank № R6986A1-1    | K     | 1216               | 1344                 | 1481             | 10.0           | 26.0            | 0.27            | 0.24            | 0.09            | 2021           |
|                       | D     | 1197               | 1334                 | 1501             | 9.6            | 30.0            | 0.27            | 0.20            | 0.08            | 2325           |
| blank № R6986A1-1    | K     | 1158               | 1305                 | 1452             | 10.0           | 23.5            | 0.27            | 0.16            | 0.10            | 2090           |
|                       | D     | 1167               | 1295                 | 1472             | 10.5           | 37.0            | 0.29            | 0.20            | 0.09            | 2403           |
Table 2. The results of periodic testing blank products 2A82-1M

| №№ | σ_p, MPa | σ_0.2, MPa | σ_s, MPa | δ, % | ψ, % | KCU +20 °C, MJ/m² | KCU −50 °C, MJ/m² | KCT −50 °C, MJ/m² | K_1C −50°C, H/mm³ |
|----|--------|----------|--------|------|------|----------------|----------------|----------------|-----------------|
| 1, 8 | 1177 | 1285 | 1393 | 9.2 | 25.0 | 0.35 | 0.22 | 0.13 | 2462 |
| | 1167 | 1285 | 1393 | 10.5 | 23.0 | 0.31 | 0.20 | 0.11 | 2629 |
| 2, 9 | 1177 | 1305 | 1413 | 8.0 | 26.0 | 0.29 | 0.20 | 0.10 | 2099 |
| | 1177 | 1305 | 1413 | 10.0 | 26.0 | 0.29 | 0.20 | 0.09 | 2207 |
| 3, 10 | 1158 | 1275 | 1383 | 8.4 | 29.0 | 0.29 | 0.20 | 0.11 | 2825 |
| | 1187 | 1295 | 1413 | 8.0 | 28.0 | 0.27 | 0.20 | 0.11 | 2639 |
| 4, 11 | 1167 | 1295 | 1422 | 10.0 | 33.0 | 0.29 | 0.20 | – | – |
| | 1167 | 1295 | 1422 | 8.4 | 24.5 | 0.29 | 0.20 | – | – |
| 5, 12 | 1177 | 1285 | 1413 | 9.6 | 32.0 | 0.27 | 0.20 | 0.11 | 2551 |
| | 1187 | 1295 | 1422 | 7.5 | 30.0 | 0.29 | 0.20 | 0.10 | 2443 |
| 6, 13 | 1187 | 1305 | 1422 | 10.0 | 30.0 | 0.31 | 0.22 | – | – |
| | 1177 | 1285 | 1413 | 9.2 | 29.0 | 0.29 | 0.22 | – | – |
| 7, 14 | 1187 | 1315 | 1432 | 9.4 | 29.0 | 0.29 | 0.22 | 0.10 | 1972 |
| | 1177 | 1305 | 1432 | 9.6 | 33.0 | 0.29 | 0.20 | 0.10 | 2580 |

From the above it is evident that all the blanks in all modes tested final heat treatment meet the requirements of National State Standard V5192-78 established for the category of strength of O-120, on indicators of mechanical properties and crack resistance, except number R6986A1-1 blanks having a value of percentage reduction below the established standard (ψ = 20%). When smelting steel billet R6986A1-1 number was excluded additive of titanium in steel for the comparative assessment of its impact on the nitrogen content and the mechanical properties of the metal blanks.

The test results of blanks №№ R6942A2-1 and R6986A1-1 by cutting along the length shows that fluctuations in the properties of the metal are observed not only at the ends of the of blanks, but also along the length. When this billet number R6986A1-1, thermally treated for mode number 2, has a uniform refractive properties throughout.

Results of control of the chemical composition of the metal of blanks are presented in table 3. The inspection results the impurity content of non-ferrous metals is presented in table 4.

Table 3. The inspection results of the chemical composition of the metal products 2A82-1M

| №№ blanks | Chemical composition, % |
|-----------|-------------------------|
|           | C       | Mn       | Si       | P       | S       | Cr       | Ni       | Cu       | Mo       | V       |
| R6942A2-1 | 0.42    | 0.26    | 0.25    | 0.012   | 0.003   | 1.04     | 3.42     | 0.22     | 0.57     | 0.16    |
| R6790A1-1 | 0.40    | 0.31    | 0.28    | 0.006   | 0.009   | 1.10     | 3.38     | 0.17     | 0.57     | 0.16    |
| R6986A1-1 | 0.39    | 0.30    | 0.32    | 0.009   | 0.007   | 1.05     | 3.39     | 0.21     | 0.58     | 0.15    |
| R7186A1-1 | 0.40    | 0.30    | 0.26    | 0.005   | 0.004   | 1.09     | 3.40     | 0.24     | 0.59     | 0.13    |
Table 4. The results of the control the content of impurities in the material non-ferrous metal products 2A82-1M

| No blanks     | Chemical composition, % |
|---------------|-------------------------|
|               | Sn | As | Pb | Sb | Zn | Bi | Al | Ti |
| R6942A2-1     | 0.009 | 0.012 | < 0.001 | 0.003 | < 0.001 | 0.002 | < 0.005 | 0.020 |
| R6986A1-1     | 0.006 | 0.012 | < 0.001 | 0.002 | < 0.001 | 0.001 | 0.010 | 0.022 |

As can be seen from the data on the chemical composition of the metal of blanks fully meets the requirements of National State Standard 5192-78. It should be noted that the metal blank number R6942A2-1 observed higher (than other metal of blanks) phosphorus content and the metal blank number R7186A1-1 is the purest on the content of sulfur and phosphorus.

Was a detailed study inclusions detected in fracture specimens for mechanical testing of selected of blanks from №№ R6986A1-1 and R7186A1-1, which had negative results on indicators of the plastic properties of metal (relative narrowing and impact toughness at room and low temperature). Type characteristic inclusions encountered in metal of blanks 2A82-1M product is shown in Figure.

Figure 1. Kind of typical non-metallic inclusions, occurring in the metal products 2A82-1M

As a result, studies have shown that the cause of lowering properties of blanks is large concentrations of nonmetallic inclusions onto the surface of the fracture. View kinks samples presented in Figures 2.

As can be seen from the photos, presented in Figure 2, on the samples taken from the work piece number R6986A1-1, inclusions were golden color, which suggests their nature nitride.

Figure 2. Kind of fracture of the sample with lowered plastic properties, selected products 2A82-1M
During metallographic studies micro sections inclusion of both types had the appearance of lines. To determine the composition of inclusions was conducted microprobe analysis, which resulted in the maps of the distribution of chemical elements contained in the inclusions. Photos inclusions micro sections and map the distribution of elements in the inclusions are shown in Figure 3 and Figure 4.

![Image](image_url)

Figure 3. Specific inclusion in the metal sample, № R6986A1-1 view of the micro section

![Image](image_url)

Figure 4. Typical inclusions in the metal sample № R6986A1-1 map the distribution of elements

The presented data show that in the absence of the titanium metal formed in the inclusions containing large amounts of calcium aluminates, and calcium and manganese sulphides. A characteristic of such impurities is that they are arranged in clusters and the layers on the primary grain boundary and lead to a decrease in the material properties, primarily plastic.

The excess of titanium contrary, leads to formation of the metal nitride and carbonitride inclusions, which are located in the metal in the form of clusters and chains extending along the direction of deformation.
As can be seen from the data, the average content of non-metallic inclusions in the metal of blanks №№ R6942A2-1 and R6986A1-1 is in the range of up to 3 points, but there were some areas (volumes of metal) of blanks, which was an increase in the content of some types of non-metallic inclusions to 4 points. The main types of inclusions - non-deformable and brittle silicates and nitrides stitch.

4. Conclusion
The results of research of mechanical properties and chemical composition comply with the requirements of National State Standard. All the blanks for all modes tested final heat treatment meet the requirements of National State Standard V5192-78. As a result, the modification does not change the basic chemical composition of the steel, but reduces the number and size of nonmetallic inclusions in the grain boundaries and also a decrease in grain size.

From the presented data it can be concluded that the modification of natural concentrates of deposits of Tomsk region has an influence on the mechanical characteristics of the resulting of blanks. The resulting research findings suggest a favorable impact of natural concentrates data on the mechanical characteristics of products.

The developed technologies allow expanding opportunities for the production of inoculants containing precious metals (Ti, Nb, Zr) by engaging in the production of natural concentrates of the Tomsk region.

References
[1] Cherepanov A N, Poluboyarov V A, Kalinin A P, Korotaeva Z A 2000 J. Materials 10 45-53
[2] Gizatulin R A, Valuev D V, Serikbol A Improving the Process Parameters Regenerative Processes at Steel Processing Ladle Furnace 2014 J. Modern Problems of Science and Education 3 1-8
[3] Fedoseev S N, Mukhtar Z M. Increasing the Operational Stability of Railway Core by Modifying 2015 J. IOP Conference Series: Materials Science and Engineering 91 (012050) 1-7
[4] Kalinin V T, Hrychikov V E, Krivosheev V A 2004 J. Metallurgical and Mining Industry 6 38-42
[5] Brover, A V Effect of Surface Heat Treatment Using of Concentrated Energy Flows on the Structural Strength of Steel 2005 J. Strengthening Technology and Coatings 4 22-25
[6] Gizatulin R A, Nokhrina O I, Kozyrev N A Steel microalloying with nitrogen by ladle bottom and top submerged lance blowing 2010 J Proceedings of Higher School Ferrous Metallurgy 6 30-33
[7] Volynova T F 1988 Metallurgy (Moscow)
[8] Fedoseev S N, Lychagin D V, Sharafutdinova A S 2014 J. Advanced Materials Research 1040 236-240
[9] Kuznetsov M A, Zernin E A, Danilov V I, Kolmogorov D E, Zubenko L N Corrosion and mechanical properties of austenic steel weld joints 2015 J. IOP Conference Series: Materials Science and Engineering 91 (012010) 1-8
[10] Rodzevich A P, Gazenaur E G, Belokurov G M 2014 J. Applied Mechanics and Materials 682 206-209.
[11] Mulyavko N M 2001 J. Proceedings of the Chelyabinsk Scientific Center 4 28-30.
[12] Illyashchenko D P, Chinakhov D A, Gotovshchik Y M Influence of power supply energy characteristics upon the stability of MMA process 2015 J. Applied Mechanics and Materials 756 97-100