Control of the properties of metal alloys obtained by aluminothermy

O N Komarov, S G Zhilin, V V Predein and A V Popov*

Institute of Machinery and Metallurgy, Far-Eastern Branch of the Russian Academy of Sciences, 1 Metallurgov Str., Komsomolsk-na-Amure, Russian Federation.

* popov.av@protonmail.com

Abstract. The paperwork considers the possibility to control the properties of the obtained experimental alloys, and also to ensure the reduction of the interaction between the resulting reaction products and materials of refractory equipment by adding filler materials to iron-aluminum thermite. There have been revealed regularities of the metal yield and the content of impurity chemical elements in the alloy composition depending on the quantity of input fillers. The analysis of the structure has been done, and hardness of the test items has been determined. The obtained experimental alloys with addition of various quantity of filler materials, according to the current standards, in chemical composition correspond to the steel grades which have been determined.

Development, implementation, and improvement of the technological processes which allow to use materials and energy resources efficiently, to reduce labor intensity of the production, and also to use production waste with maximum efficiency is a strategic goal of industrial enterprises [1-5]. This considerably relates to the enterprises which are involved in production and processing of metal and metal products and consume a vast number of materials and energy resources. The usage of modern technologies provides reduction of final product costs that ensures reduction of its cost production and increase of competitiveness.

In the foundry industry in the sector of casting production, the use of thermite materials is the technological solution that solves the economic problems. It allows to obtain castings fully made from alloys resulted in exothermic reaction flowing in thermite mixtures. Thermite mixtures consist of scale (complex of iron oxides) and ground chips of aluminum alloys, in a certain ratio. To control the exothermic reaction, the chemical composition and the properties of the castings obtained, various ferroalloys, filler materials and other components are added to the thermite compounds [6-8].

High temperatures of exothermic reactions, which form the basis of the technologies for casting manufacturing with the use of thermite compounds, in some cases, restrain their widespread implementation into production. First, one of the main reasons is the difficulty in determining the product reaction temperatures; as a result, the metal is poured into the mold without control of pouring temperature that affects the quality of cast blanks. Secondly, high temperature leads to increased gas generation and increases the irretrievable loss of materials. In addition, high temperature of the reaction products intensifies the interaction between them and the refractory equipment, reducing the lifetime of the latter, which leads to uncontrolled saturation of the resulting metal phase with impurity elements. Thuswise, using carbon crucibles and molds the formed metal phase is intensively saturated with carbon
and the usage of magnesia refractories increases the amount of slag phase [10]. To reduce temperature of the reaction products while producing the aluminothermic alloys with the required properties it needs to add to the thermite compound the following fillers: chips of ferrous, ferroalloys. Fillers can solve some of the problems noted above and increase the yield of the metal phase. However, the addition of fillers to thermite compositions is possible only up to a certain amount. Their excess leads to a decrease in the temperature of the reaction products to a level at which the separation of metal and slag becomes difficult.

Having regard to the abovementioned, the purpose of the work is to determine the influence of fillers added to the composition of the thermite compounds on the yield of the thermite metal, its structure, properties, and also the correspondence of the chemical composition of the experimental alloys to grade alloys.

To achieve the purpose of the research, the following tasks have been carried out:

- To determine the regularities of influence of the amount of fillers added to the thermite composition on the yield of the resulting experimental;
- To determine the regularities of influence of the amount of fillers added to the thermite charge composition on the chemical composition of the resulting metal phase;
- To study the structure of experimental alloy samples;
- To determine the hardness parameters of experimental alloy samples.

The conducting of exothermic reaction was carried out in refractory crucibles made from ЭГ15 graphite electrode scrap used for steel melting in electric arc furnaces in accordance with ТУ 14-139- 177-2003 Technical Specifications «Graphite electrodes of diameter from 75 to 555 mm and nipples for them. Technical specifications». The density of the refractory material was 1700 kg/m3. The working space volume of the crucible was 0.000572 m3, the wall thickness was 0.01 m. The weight of the crucible was 0.71 kg. The volume of the working space corresponded to the charge of compound of 1 kg with a minimum bulk density (without compaction) to obtain a sample of the required size. The crucible after the compound charge was covered with a lid having a hole for the gases output (diameter is 20 mm). The inner diameter of the crucible was equal to the height of its working space and was 0.09 m. A one-time-use insert with a hole of 0.007 m in diameter was installed in the bottom of the crucible to stabilize the melt casting speed. The metal drainage hole was closed with EG15 graphite cone plug. After passing the reaction and dwelling the melt in the crucible for 10 seconds (to ensure the separation of metal and slag), the plug was knocked out, the mold was filled with metal. The mold for obtaining the samples was a deaf-bottomed cylinder, with an internal diameter of 0.03 m, wall thickness of 0.03 m and height of 0.15 m. Before starting the experiments the refractory equipment was heated up to 150 °C and was coated with parting paint of the following composition: marshallit – 20 %, liquid glass – 5 %, water – 74 %, boric acid – 1 %.

Iron-aluminum thermite compound consisted of components the fraction of which was 0.2 – 1.5 mm and its chemical composition was the following: reducer – Al = 98.627 %; Cu = 0.018 %; Si = 0.855 %; Mn = 0.019 %; Fe = 0.462 %; Cr = 0.016 %; Ni = 0.004 %; iron scale – Fe = 71.500 %; O2= 22.639 %; Si = 2.960 %; Mn = 1.188 %; Al = 0.697 %; Cu = 0.444 %; Ni = 0.188 %; Cr = 0.173 %; C = 0.150 %; S = 0.030 %; P = 0.030 %; FMn-78(A) ferromanganese of fraction up to 0.04 mm, which corresponds to the requirements of GOST 4755-91 «Ferromanganese. Technical requirements and terms of delivery», with chemical composition: Mn = 78.050%; C = 6.990%; Si = 0.790%; S = 0.008%; P = 0.189%; steel alloy grits (St3sp steel grade according to GOST 380-2005) of fraction of 1-3 mm with chemical composition: C = 0.180%; Mn = 0.520%; Si = 0.210%; S = 0.021%; P = 0.028; Ni = 0.010%; Cr =0.110%; Cu = 0.220%.

Preparation of thermite compounds was carried out by blending in a mixer for 10 minutes; drying at 150 °C for 1 hour; re-blending for 10 minutes, during which homogenization of the mixture is achieved and partial crushing of the components lead to the cleaning of the surface of the reducing agent particles from the oxide film and the ensuring the intensive interaction between the reacting particles.

The chemical composition of the samples was determined with the help of Q4 TASMAN 170 BRUKER optical emission spectrometer. To specify the metal structure of the castings, microscope
AXIO VERT A1 with camera AxioCam ERC5s was used. To determine the hardness of the thermite metal, Rockwell scale (HRC) was used. Then the values were converted into Brinell scale to simplify the comparison of properties of the experimental alloys with the properties of the alloys produced with traditional methods. To determine the hardness of the experimental alloys, TK-2M stationary hardness measuring instrument with diamond spherocical penetrator was used.

The analysis of the experimental data has been revealed that the content of the used reducer contained in the thermite composition taking into account the amount of residual aluminum in the melts, the yield of the metal phase and the quality of the samples obtained under the initial standard temperature conditions of the charge and molds, is 22%. All the experimental charges were composed on the base of the thermite with the reducer content of 22%. The composition of the compounds used during the research is shown in Table 1.

### Table 1. Composition of the compounds used

| №  | Materials                  | Content of components in the thermite, % | Charge №1 | Charge №2 | Charge №3 | Charge №4 | Charge №5 | Charge №6 | Charge №7 |
|----|----------------------------|-----------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1. | Reducer                   |                                         | 22        | 22        | 22        | 22        | 22        | 22        | 22        |
| 2. | Scale                     |                                         | 78        | 78        | 78        | 78        | 78        | 78        | 78        |
|    | Total, %                  |                                         | 100       | 100       | 100       | 100       | 100       | 100       | 100       |
| 3. | FMn78(A) (Ferromanganese) |                                         | 0         | 2         | 2         | 2         | 2         | 2         | 2         |
| 4. | Steel grits of St3sp grade steel |                                   | 0         | 0         | 15        | 30        | 45        | 60        | 75        |
|    | Total, g./%               |                                         | 0/0       | 2/0,2     | 17-1,6    | 32-3      | 47-4,3    | 62-5,6    | 77-6,5    |

The research has been revealed that the yield of the metal phase with the addition to the compound of fillers in the form of FMn78 (A) ferromanganese and St3sp steel grits increases proportionally to their content in the compounds of 4.3%. Also there is a maximum yield of thermite metal, it is 53.24%. In fig. 1 shows the dependence of the yield of thermite metal on the content of fillers in the alloy. Figure 1 shows the dependence of the thermite metal yield on the content of the fillers in the alloy.

![Figure 1](image-url)
The increase in the volume of the formed metal phase is explained by the fact that the calorific value of thermite is sufficient for the reaction of all iron oxides with a reducer complete melting of fillers and their transition into the metal. The addition of these components over 4.3% reduces the calorific value of thermite compound, affecting the temperature of the reaction products. The conditions for intensive oxidation of certain chemical elements are being formed. At the same time, bringing the amount of fillers in the compositions to 5.6% and 6.5% provides the yield of thermite metal of 52.71% and 52.02%, correspondingly. The reduction of the thermite metal yield is due to a decrease of carbon absorption by the alloy when it interacts with the refractory equipment, which is determined by the decrease in the average temperature of the exothermic process.

It has been experimentally determined that a change in the temperature of the reaction products controlled by the introduction of fillers, leads to a change in the behavior of impurity chemical elements capable to oxidize, to recover, and burn off. The sequence can be any: depending on the state of the elements distributed between the metal, slag and gas phases. Exothermic reactions are transient, therefore, in most cases, the equilibrium content of elements in these phases is not achieved. In general, the modes of obtaining experimental alloys are significantly different from the conditions for the metal production by traditional methods [11]. Figure 2 shows the dependence of the content of impurity elements in the resulting alloys on the content of fillers in mixtures.

The reduction of temperature of the reaction products declines the upper carbon level content in the experimental alloys. The studies have found that the carbon content in the resulting materials is reduced from 1.99% to 0.38% over the entire range of the content of added fillers 0.2 ÷ 6.5%. Partial decrease of carbon content with the addition of fillers in the amount of 0 ÷ 4.3% in the resulting alloys is explained by an increase of the metal phase and a dilution of carbon concentration. The addition of fillers into the thermite compound in the amount of 5.6% and 6.5% reduces the carbon content in the metal phase to 1.32% and 0.38%, correspondingly.

The content of manganese in the studied alloys mainly depends on its content in the initial charge materials. The low absorption of manganese from the initial components of the charge materials is explained by the high temperature of the reaction products, which leads to an increase of the partial pressure of manganese vapor and its transition to the gas and slag phases. The increase in the content of
manganese in alloys from 0.24% to 0.29% is due to the increase in its content of fillers on adding the fillers in the amount of 1.6 ÷ 3%. Then its content is reduced to 0.28%; it is connected with an increase in the iron content due to an increase in the amount of fillers added to the compound in the range of 4.3–5.6%. The maximum content of manganese in the alloys of 0.32% is observed with the addition of fillers into the composition in the amount of 6.5%, due to a decrease in the average reaction temperature and a decrease in the yield of the metal phase to 52%.

The amount of silicon increases to a maximum value of 0.28% due to an increase of the input fillers up to 1.6%. The fillers added over 3 ÷ 4.3% provide an increase in the metal phase yield, which dilutes the Si concentration to 0.26% and 0.24%, respectively. Further increase of fillers does not change the content of Si in the alloys and is equal to 0.24%, which is compensated by a decrease of the overall yield of the metal phase and an increase of the rate of Si oxidation with a decrease of temperature.

The chromium content in the studied alloys varies slightly over the entire range of input fillers and is 0.05%. This is mainly due to the fact that the chromium content in all initial components is the same and, changing their ratio, the amount of chromium in the compositions remains at the same level. The increase in the chromium content in the metal phase is compensated by its increase, as well as by the oxidation of Cr on adding to the thermite compositions from 5.6 to 6.5% of fillers, which reduce the temperature of the reaction products.

The copper content in the original components is the same and changing their ratio, the amount of copper in the compositions remains at the same level. If the content of the fillers in the compounds is up to 1.6%, an increase of the content of Cu in the alloys is up to 0.16%. This happens due to a decrease of the temperature of the reaction products, when there is a significant decrease in the pressure of Cu vapors and a reduction in their removal to the gas and slag phase. Adding fillers to the compound of 1.6 ÷ 5.6%, the copper content remains at the level of 0.16%. When the content of fillers in the composition of mixtures is 6.5%, the amount of Cu in the melt is 0.17%. A slight increase of Cu content is determined by a decrease of the thermite metal yield and a decrease of the average temperature of the reaction products.

The nickel content in the resulting alloys is limited by the temperature effect of the resulting reaction products. If the content of fillers in mixtures is from 0% to 3%, the amount of nickel is 0.1%. The range of fillers content of 3 ÷ 4.3% increases the amount of nickel in the alloy to 0.11%, which is maintained up to 6.5% of the added fillers in the mixture. In this range, the total deficiency of nickel decreases and its content in the alloys increases.

Along with carbon, aluminum is the most dependent on the temperature of the reaction products element in the obtained experimental alloys. In general, an increase of the aluminum content is observed in the entire range of fillers added to the thermite mixture, and it determines the average temperature of the reaction products. The content of residual aluminum with an increase of added fillers is 0.085 ÷ 1.02%. The increase of the aluminum content in the melt, due to a decrease of the temperature of the reaction products, is limited by general increase of the metal phase only by adding 3% of fillers in the mixture, where there is a slight decrease of its amount from 0.26% to 0.22%. The maximum increase of the aluminum content in the alloys occurs in the range of added fillers in the thermite composition in the amount of 5.6 ÷ 6.5%, and the aluminum content changes from 0.44% to 1.02%.

The sulfur content in the resulting alloys increases from 0.013% to 0.038% when fillers are added in the amount of 0 ÷ 6.5%. The amount of sulfur in the alloys does not actually change up to 5.6% of the content of fillers in thermite mixtures, which is determined by the increase of the total mass of the metal phase. In the range of the content of fillers in mixtures 5.6 ÷ 6.5%, there is a surge in the sulfur content in the alloy, due to a decrease in the metal phase yield and a decrease in the average temperature of the reaction products. Sulfur, having a low boiling point, rapidly evaporates into the gas phase, and partially settles in the slag. Therefore, a decrease of the temperature of the reaction products leads to an increase in the sulfur content in the alloys.

The change in the phosphorus content in the experimental alloys depends on the temperature of the reaction products, which is regulated by adding the fillers into the melt. Intensive growth of the phosphorus content in alloys up to 0.027% is observed when 1.6% of fillers are added to the mixture.
When the content of fillers in the mixtures is 3%, the content of phosphorus is reduced up to 0.026% with an abrupt increase in the yield of the metal phase. An accelerated decrease of the phosphorus content in the alloys is observed when the content of the fillers is 5.6 ÷ 6.5% due to the temperature of the reaction products, under which the phosphorus is oxidized and transits into the slag phase.

Using the abovementioned charge materials, it is possible to obtain alloys the chemical composition of which correspond to chemical composition of the grade alloys. Table 2 shows the chemical compositions of the experimental alloys and of the grade alloys.

**Table 2.** The correspondence of chemical composition of the experimental alloys to chemical composition of the grade alloys

| № | Elements | Content of chemical elements in the alloys, % | Chemical composition |
|---|----------|---------------------------------------------|----------------------|
| 1 | C        | 1,990 1,930 1,870 1,830 1,830 1,800-2,800| 1,320 1,260-1,340 0,380 up to 0,400 0,360-0,890 |
| 2 | Mn       | 0,230 0,250 0,290 0,290 0,280 No specified | 0,280 0,170-0,330 0,320 up to 0,800 0,240-1,560 |
| 3 | Si       | 0,260 0,250 0,290 0,290 0,260 0,240 | 0,240 0,170-0,330 0,240 up to 0,500 0,070-0,380 |
| 4 | S        | 0,017 0,015 0,017 0,016 0,016 No specified | 0,017 up to 0,028 0,038 up to 0,040 up to 0,048 |
| 5 | P        | 0,021 0,017 0,027 0,026 0,027 0,027 | 0,027 up to 0,030 0,020 up to 0,040 up to 0,048 |
| 6 | Cr       | 0,050 0,050 0,050 0,050 0,050 0,050 | 0,050 up to 0,200 0,050 up to 1,200 - |
| 7 | Ni       | 0,100 0,100 0,100 0,100 0,110 0,110 | 0,110 up to 0,250 0,110 - - |
| 8 | Cu       | 0,14 0,15 0,16 0,16 0,16 0,16 | 0,160 up to 0,250 0,170 up to 0,300 - |
| 9 | Al       | 0,07 0,08 0,26 0,22 0,32 0,440 | 0,085 0,26 0,22 0,32 0,440 1,020 - - |

1. C 1.260 ÷ 1.340
2. Mn 0.170 ÷ 0.330
3. Si 0.170 ÷ 0.330
4. S 0.017 ÷ 0.028
5. P 0.027 ÷ 0.030
6. Cr 0.050 ÷ 0.200
7. Ni 0.110 ÷ 0.250
8. Cu 0.160 ÷ 0.250
9. Al 0.085 ÷ 0.440

*aAccording to GOST 21427.1-83; According to GOST 1435-74; **According to GOST 31334-2007; **According to GOST 50567-93
The alloys obtained from thermite charge №1 и №6, are characterized by heterogeneity of the structure, which requires heat treatment corresponding to the type of alloys with similar chemical composition. The alloy obtained from composition № 7 has the structure of martensite, which is achieved by using heat treatment [12] during traditional processes of cast blank production, and further it is planned to be excluded. The microstructure of test specimens produced from thermite charge №1, is shown in Figure. 3.

Widmanstätten structure (Thomson structure) corresponds to as-cast condition and is typical for cast blanks obtained during the crystallization with high speed of undercooling. Secondary cementite is released from austenite in the form of plates (on the plane of thin section in the form of needles), oriented relative to the austenite lattice. The matrix is perlite with plates of various sizes and residual austenite. The grain size is difficult to define. The average hardness of the specimens is HRC 44.8 (~ 427 HB).

The microstructure of test specimens produced from thermite charge №6, is shown in Figure. 4. The structure corresponds to as-cast condition, fine-grained, the size of grain is of 7 points according to GOST 5639-82. There are colonies of perlite with a well-distinguishable lamellar structure up to 5 points according to GOST 8233-56. Cementite is released from austenite in a structurally free form, and is of 4 points according to GOST 5640-68. The average hardness of the specimens is HRC 38 (~ 352 HB).
Microstructure of the test specimens produced with the use of thermite charge №7 is shown in Figure 5. The structure corresponds to as-cast condition. The main microconstituent is martensite. The size of grain is up to 10 points according to GOST 833-56. The average hardness of the specimens is HRC 3.6 (~169 HB).

Figure 5a. Microstructure of the test specimen produced with the use of thermite charge №7 zooming x200

Figure 5b. Microstructure of the test specimen produced with the use of thermite charge №7 zooming x1000.

Adding of various fillers to thermite compositions allows to reduce the reaction temperature and to increase the yield of the metal phase. Reduction of temperature of the resulting reaction products allows to control the absorption of useful and injurious impurity elements, which makes it possible to obtain grade alloys. Reduction the temperature of the reaction products also reduces the intensity of their interaction with the refractory equipment in molds and crucibles, increasing their durability. It also becomes possible to control the processes of metal crystallization that ensures the production of cast blanks with the required level of internal stresses and the required microconstituents. Thus, the addition of fillers in compounds with high calorific value leads to an overall positive effect.

Acknowledgments
The work has been carried out within the state assignment № 075-00414-19-00.

References
[1] Garilin I V 2004 The technology of remelting waste and zinc oxides Metallurgy engineering № 6 27-28.
[2] Tokmin A M and Bykonya L A 2006 Microalloying and modification of die steel produced using electroslag technology Metal technology. № 4. 25-31
[3] Gorelov V G, Kireev Y V and Shevlyakov A V 1993 The use of powdered waste in the steel smelting Foundry production. № 10. 33-34.
[4] Babaytsev I V, Osadchiy V B and Rytikov A M 1993 Effective use of wastes of foil production Non-ferrous metallurgy. № 2. 63-64.
[5] Safronov N N, Safronov N G and Kharisov L R 2013. Thermite mixture for gformation of granules used for the oxidasing refining of iron-carbon alloys. Pat. № RU2480518.
[6] Novokhatskii V A, Zhukov A A and Makarychev Y I 1986 Low-waste technology for production of steel castings with exothermic risers (Moscow: Mechanical engineering) p 64
[7] Komarov O N, Zhilin S G and Sapchenko I G 2008 The use of thermite materials in the technology of production of steel castings (Vladivostok: Dalnauka) p 166
[8] Komarov O N, Zhilin S G, Evstigneev A I, Potyanikhin D A, Predein V V, Abashkin E E, Popov A V, Ri Khosen, Panchenko G L 2018 Device for producing iron-carbon-alloy castings. Pat. № RU2658682

[9] Komarov O N 2018 Effect of production factors in aluminothermy on properties of received castings from experimental alloys Scholarly Notes of Komsomolsk-na-Amure State Technical University. 1, № 3(35) 56-65.

[10] Krasnyi B L, Tarasovskii V P, Krasniy A B, Enko A S 2007 Development of heat-resistant refractory material based on periclase and spinel for the manufacture of crucibles used in aluminothermic welding of rails. Refractories and technical ceramics.. № 10. 3-8

[11] Bigeev A M 1988 Steel metallurgy (Chelyabinsk.: Metallurgy, Chelyabinsk department,) 480.

[12] Gulyaev A P 1978 Metal science (Moscw.: Metallurgy) 648.