Structure and properties control of carbon alloys cast blanks produced by aluminothermic method with following heat treatment

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

Khabarovsk Federal Research Centre of the Far Eastern Branch of the Russian Academy of Sciences, 1, Metallurgov street, Komsomolsk-na-Amure, 681005, Russia.

*sergeyzhilin1@rambler.ru

Abstract. Casting production with aluminothermic method is one of the mainstream lines of production process designing and improvement in foundry practices. Cast blanks production methods based on thermite mixtures application provide economic benefits due to machinery and steel production plants waste (ferrous and non-ferrous chip scrap and scale) usage. Alloys resulting from exothermal reaction are used for cast blanks production. For minimization of expenses coming from power consumption, the oncoming cast blanks properties correction is conducted at initial stages to put them into operation immediately after production, which is achieved by adding fillers in charge materials to decrease reaction’s heating effect or by external heat supply. In some cases reaction’s high intensity and temperature lead to difficulties in final properties foreseeing therefore affecting the formation of repairable and irreparable defects. Cast blanks with irreparable defects are used as charge materials in further recasting in traditional melting units, which increases metal waste processing efficiency and non-wastefulness. Cast blanks with repairable defects are a subject to further processing. E.g., in case of chemical and structural inhomogeneity, high-rate internal stress, cast blanks are a subject to complex heat treatment, that allows bringing properties to the required level. Annealing is applied to achieve better homogeneity compared to as-cast condition. After heat treatment cast blanks contain granular pearlite or ferrite with various inclusions. It’s been established that high rates of alloying aluminium increase the high-carbon steels hardening temperature. After 1000°C hardening the samples have martensite structure with hardness index up to 628 HBW.

1. Introduction

Introduction of new technological processes and improvement of current ones establish enterprises’ release of products having competitive advantages, such as high quality and low cost. At the same time, new technological operations practicing in order to obtain required product types takes a prolonged period of time and may lead to obtaining products significantly deviating from required properties, which may result in product rejection. Aluminothermy is an unconventional method in metallurgy and foundry practices, which is applied to iron-carbon alloys and castings produced of them and which exhibits some undeniable advantages to the existing methods in respective industries [1, 2]. First of all, aluminothermy contributes to metallurgy and machinery plants’ slag disposal areas reduction that determines environmental improvement. Secondly, due to exothermal reaction’s high heating effect in thermite mixtures it reduces the consumption of energy resources, which are a
significant part of product cost [4]. Thirdly, alloy production and, thus, cast blanks production process cycle time reduces due to above-mentioned reactions high intensity [5]. Aluminothermy is determined by reaction products high temperature and intensive thermite mixtures components interaction, which contributes to intensive mechanical and diffusive mixing of the melt. [6]. In concurrence with this, high temperature gradient is formed between a poured melt and a mold, leading to high internal stress formation and hardening structures emerging [7]. When applying aluminothermy as a cast blanks production method, it’s essential to provide conditions for exothermal reactions which allow achieving the cast blanks required properties. Properties correction is conducted in 2 directions: thermite mixture calorific effect reduction by non-reactive additive induction; additional heat induction by preheating. [8]. Additives induction and thermite mixtures preheating application allow to control reaction intensity, poured metal temperature, its chemical composition, components uniformity and alloy yield. All this factors combined determine the formation of homogeneous structure and casting properties. When applying identical mixtures it is possible to adjust the chemical composition and obtained alloys properties by process factors changing, particularly by thermite mixtures preheating over the temperature range of 25-600°C [9, 10]. Therefore it makes it possible to obtain cast blanks structure and properties not requiring further correction. Nevertheless, like conventional casting production methods, aluminothermy has its own disadvantages in providing required quality. Cast blanks defects may be repairable and irrepairable. Cast blanks with irrepairable defects are used as charge materials in further recasting in traditional melting units. Repairable defects, particularly chemical and structural inhomogeneity, high-rate internal stress in cast blanks are corrected by heat treatment application. Concurrently heat treatment is used not only for defects repair, but also for cast blanks required properties.

Thus, the purpose of this work is to determine the heat treatment variations effect on structure and properties of the obtained samples.

In the framework of the research, the following tasks were solved:
- to obtain the experimental samples from iron-carbon alloys using the aluminothermy;
- to conduct microstructural analysis for the samples obtained from experimental alloys;
- to specify hardness for the samples obtained from experimental alloys;
- to specify experimental samples heat treatment effect on their structure and hardness.

2. Experiment description
The exothermic reaction was conducted in the 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 to obtain a sample of the required size. After the compound charge, the crucible was covered with a lid having a hole for the gases output (diameter of 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 ЭГ15 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 and 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 equipments was heated up to 150 ºC and was coated with parting paint of the following composition: marshallit – 20 %, liquid glass – 5 %, water – 74 %, boric acid – 1 %.

Preparation of the initial components of the thermite mixtures consisted of preliminary grinding and separation on testing sieves. Iron-aluminum thermite mixture consisted of components the fraction of which was 0.2 – 1.5 mm and its chemical composition was the following: reducing agent
(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 %). The experimental mixture used in the work consisted of 25% of the reducing agent and 75% of iron oxides without fillers.

Preparation of the 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 and partial crushing of the components were achieved and led to the cleaning of the surface of the reducing agent particles from the oxide film and the ensuring of the intensive interaction between the reacting particles. The resulting thermite mixtures were placed into the graphite crucibles (before initiation of the reaction, the crucible – mixture system had temperatures of 25°C, 200 °C, 400°C, 600°C). The heating up to the temperatures different from standard conditions was carried out in SNOL 12/1300 thermite resistance furnace of muffle type.

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 thermite metal hardness universal hardness measuring instrument Metolab 703 with a diamond cone indenter was used by the Rockwell method (HRC) with following conversion to Brinell scale (HBW).

Heat treatment of samples produced of experimental alloys was performed in SNOL 12/1300 electric lab furnace. Underannealing mode: heating at the rate of 10°C/min for 76 minutes up to 760°C, soaking at this temperature for 720 minutes, cooling at the rate of 0.8°C/min for 592 minutes down to ambient temperature. Diffusive annealing mode: heating at the rate of 10 °C/min for 110 minutes up to 1100°C, soaking at this temperature for 720 minutes, cooling at the rate of 0.8°C/min for 1260 minutes down to ambient temperature. Hardening at 830°C and 1000°C. Estimated soaking time – 8 minutes and cooling in water. Low-temperature tempering was performed by samples soaking in the furnace at 180°C for 40 minutes with following cooling in water.

3. Experiment results

Studies discovered that pre-heating of the thermite compositions in the temperature range of 25-600 °C significantly affects the content of elements in the experimental alloys such as carbon, aluminum, manganese, silicon. The quantity of other impurities in the resulting metals in the temperature range of the thermite mixtures under consideration does not change significantly. Thermite mixtures initial temperatures define reaction products temperatures. Concurrently with temperature increase above 200°C, the thermite metal yield reduces, gas and slag constituents increase, interaction between carbon pattern equipment and reaction products, which leads to melts carbon saturation with moldings and crucibles durability decrease. Proceeding from results analysis, the initial temperatures above 400°C before process start is unpractical due to significant alloy mass yield reduction. Table 1 catalogs chemical elements content and amount of their yield depending upon the thermite mixtures initial temperature.

| Mixtures heating temperatures, °C | C  | Mn  | Si  | S  | P  | Cr  | Ni  | Cu  | Al  | Metal yield, % |
|----------------------------------|----|-----|-----|----|----|-----|-----|-----|-----|----------------|
| 25                               | 1.450 | 0.910 | 0.720 | 0.016 | 0.025 | 0.070 | 0.120 | 0.200 | 5.290          | 52.820          |
| 200                              | 1.320 | 0.900 | 0.760 | 0.018 | 0.025 | 0.060 | 0.110 | 0.200 | 5.220          | 53.920          |
| 400                              | 1.510 | 0.840 | 0.800 | 0.019 | 0.022 | 0.060 | 0.110 | 0.180 | 4.040          | 50.470          |
| 600                              | 1.660 | 0.620 | 0.700 | 0.016 | 0.024 | 0.060 | 0.110 | 0.170 | 4.330          | 41.370          |
Metallic phase chemical composition along with its temperature before being poured into a mold, pouring rate and mold temperature determine experimental samples structure and properties. The significant difference in cast blanks structures obtained from thermite metal under the condition of initial thermite compositions unity, during their initial temperature changes conforms to the temperature and time conditions changes for crystallization and casting cooling in a mold. The structures conform to as-cast condition. Troostite and plate martensite localized areas with retained austenite characterize the structure of the sample obtained without thermite composition preheating. The sample obtained with thermite composition initial temperature of 200°C contains troostite with secondary cementite areas of different size in its structure. The sample obtained with thermite composition initial temperature of 400°C contains plate martensite with a small quantity of retained austenite and spheroidal graphite presence. In case of composition heating up over 600°C plate martensite emerges in samples structure along with a bigger, compared to previous samples, amount of non-transmutated austenite. Concurrently there may be observed undissolved spheroidal graphite presence. All samples are high-carbon – 1.32-1.66%. For high-carbon hypereutectoid steels underannealing is basically applied in order to relieve internal stress, which allows obtaining granular pearlite [11, 12]. Granular pearlite structure is typical for tool steel without hardening that provides better machinability and low hardness. The samples obtaining granular pearlite have higher viscosity and strength after hardening due to hardening optimal temperature decrease and austenite grain size reduction that contributes to the tool service properties improvement.

760°C annealing provided granular and plate ferrite-matrix pearlite (dispersity rate: 6 points (medium-sized grain) and 9 points (big-sized grain) respectively, according to GOST 8233-56) formation in the structure of the samples obtained from thermite mixtures having initial temperature of 25°C and 200°C. Meanwhile, granular and plate pearlite ratio is 85% to 15% respectively. The structures of the samples obtained from thermite mixtures at the temperature of 400°C and 600°C consist of the ferrite with grain size corresponding to 6 and 7 points respectively as well as cementite clusters, other carbides, graphite and various content compounds. Figure 1 demonstrates the examples of structures of the samples obtained with thermite mixtures initial temperatures of 200°C and 400°C after 760°C underannealing.

![Figure 1](image1.png)

**Figure 1.** Structures of the examples obtained with thermite mixtures initial temperatures of 200°C and 400°C after underannealing (x1000): a - 200°C; b - 400°C.

To exclude alloys composition inhomogeneity additional 1100°C diffusive annealing was applied to samples, followed by 830°C hardening with low-temperature tempering. Based on heat-treated
metallographic sections analysis results, it was established that the samples obtained from application of mixtures having initial temperature of 25°C and 200°C demonstrate granular and plate pearlite presence in ferrite matrix with respective estimated dispersity rate of 6 and 5 points (according to GOST 8233-56), also cementite is observed at the grain boundaries. The samples obtained from thermite mixtures with initial temperatures of 400°C and 600°C have homogenous ferrite structure with cementite and graphite appearing at the grain boundaries, with grain size corresponding to 7 points according to GOST 5639-82. Figure 2 demonstrates the examples of structures of the samples obtained with thermite mixtures initial temperatures of 200°C and 400°C after 1100°C diffusive annealing followed by 830°C hardening and water cooling. Low-temperature tempering was applied to relieve internal stress. After diffusive annealing all samples demonstrate external layer emergence up to 3 mm. This layer is different in composition, structure and properties from sample central area. Figure 3 demonstrates the sample which shows peripheral area of reduced etchability. At this area principal elements content is reduced: carbon – by 38%; manganese – by 11%; silicon – by 31%; aluminium – by 38%. Big-sized grain area with the structure elongated from sample centre to edge is shown at figure 4. Its hardness after heat treatment operation complex is reduced by 25% compared to core metal.

It’s been established during research that 830°C hardening with water cooling and following low-temperature tempering doesn’t allow to obtain traditional martensite structure in experimental samples containing more than 1,32% of carbon. Supposedly, it is explained by high aluminium content. 1000°C hardening with water cooling and following 180°C tempering contributed to obtaining martensite without austenite retained in central area of each sample. In the structure of the samples obtained with thermite mixture initial temperature of 200°C may be found insignificant amount of isolated cementite clusters affecting their hardness. Due to specific composition and structure, the peripheral area, virtually, is not apt to hardening and significant properties changing. Transition area is represented by ferrite, granular and plate pearlite of various dispersity. Figure 5 demonstrates central and transition area microstructures of the samples after diffusive annealing with following hardening and low-temperature tempering.

Figure 2. The samples structures obtained from thermite mixtures different initial temperatures after diffusive annealing, hardening and low-temperature tempering (x1000): a - 200°C; b - 400°C.
The structures forming after heat treatment, as well as experimental samples chemical composition, affect hardness. Samples hardness changing dynamics in as-cast condition with initial temperatures of applied mixtures ranging from 25°C to 400°C is comparable to carbon content changing dynamics of alloys. The deviation of thermite mixtures with initial temperature of 600°C from carbon content changing curve of alloys is determined by thermite metal yield along with crystallization mode change and metal cooling in a mold. 760°C underannealing contributed to internal stress relief and hardness reduction by 54% to 70% in all samples due to structural constituents changing. Concurrently, hardness changing dynamics corresponding to samples as-cast condition retained. The application of diffusive annealing, 830°C hardening with water cooling and low-temperature tempering determined hardness changing dynamics in central and peripheral areas. Along with that the insignificant difference between their hardness indexes. The samples obtained with mixtures initial temperature of 25-200°C are distinguished by central area increased hardness due to retaining of granular pearlite in its structure during heat treatment, its (granular pearlite’s) dispersity reduction and partial transition into plate pearlite. Insignificant change of samples hardness in the range of 181 to 211 HBW is observed in peripheral area, depending upon thermite mixture initial heating temperature. 1000°C hardening with water cooling and low-temperature tempering operations allowed to obtain martensite in central areas of all samples and to increase samples hardness to 567-628 HBW. Hardness changing dynamics is comparable to previous heat treatment operation. With identical samples structural constituents, hardness changing is connected to different chemical composition of alloys and martensite dispersity. Central area hardness maximum increase in the sample obtained with the thermite mixture initial temperature of 200°C is connected to a small amount of cementite in it. Peripheral area hardness remained almost the same, compared to previous heat treatment operations, in the range of 178-200 HBW. Figure 6 demonstrates thermite mixture initial heating temperature and heat treatment types effect on samples hardness changing.
Figure 5. Structures of the samples obtained with thermite mixture initial temperature of 400°C after diffusive annealing, hardening and low-temperature tempering: a – transition area (x200); b – central area (x1000).

Figure 6. Hardness of samples obtained with mixtures different initial temperature, depending upon heat treatment method: a – no heat treatment; b – 760 °C annealing; c – 830°C hardening with water cooling and low-temperature tempering (central area hardness); d – 830°C hardening with water cooling and low-temperature tempering (peripheral area hardness); e – 1000°C hardening with water cooling and low-temperature tempering (central area hardness); f – 1000°C hardening with water cooling and low-temperature tempering (peripheral area hardness).
4. Conclusion
Thus, thermite mixtures preheating application before exothermic reactions allows to obtain alloys having different chemical compositions, structures and properties in as-cast condition. 760°C underannealing allowed obtaining structure constituents and size changing in tested samples that determined hardness reduction to 70%. 1000°C diffusive annealing for 12 hours leads to samples surface decarbonization and aluminium content reduction which result in formation of 3 mm. external layer with the structure and properties different from central area. 830°C hardening contributes to hardness increase in central areas of cast blanks obtained with thermite mixtures initial temperatures of 25°C and 200°C due to granular pearlite dispersion and partial transition into plate pearlite. Granular pearlite in the samples emerged during underannealing operations and retained after. Concurrently, underannealing of the samples obtained with thermite mixtures initial temperature of 400°C and 600°C formed their ferrite structure after martensite recrystallization. Despite high-carbon content in the samples, significant aluminium concentration pinches out the γ-zone and creates the conditions for the formation of ferrite whose transition into austenite is possible with the hardening temperature over 830°C. 1000°C hardening allowed achieving martensite structure formation (in central areas of all samples) and reaching the hardness value of 628 HBW. Traditionally high-carbon tool steels are hardened with 760-780°C temperature for martensite formation in cast blanks structure. In this basis, aluminium high content in the composition increases high-carbon steel hardening temperature. Regardless of heat treatment mode, peripheral layer consists of big-sized ferrite grains elongated from the centre; its hardness is at the range of 178 – 211 HBW. For all practical purposes, the presented cast blanks production method with following heat treatment makes it possible to obtain bimetallic items with ductile external layer and hard centre which may be applied for high-strength construction elements manufacturing including those subjected to welding.

References
[1] Beckert M. Neumann A. Grundlagen der Schweißtechnik - Schweißverfahren. Berlin: VEB Verlag Technik. 1974.
[2] Novokhatskiy V.A., Zhukov A.A., Makarychev Yu. I. Low-waste technology for exothermic hot tops steel casting production // Mashinostroeniye, Moscow, 1986.
[3] Popov A.V., Komarov O.N., Predein V.V., Zhilin S.G. Nondestructive evaluation of the service life of casting products made of thermite alloys // AIP Conference Proceedings Proceedings of the 12th International Conference on Mechanics, Resource and Diagnostics of Materials and Structures. 2018. C. 040076.
[4] Golovchenko N.Yu., S.Kh. Aknazarov, G.I. Ksandopulo, A. Mukasyan Extraction of ferrotungsten from the oar with low WO3 concentration// ISSN 1061-3862 International Journal of Self-Propagating High-Temperature Synthesis.Russia.- 2012, vol. 21. № 3, Р. 156-161.
[5] Karguin, V.A., Tikhomirova, L.B., Galay, M.S., Kuznetsova, Ye.S., Improving service properties of welded joints produced by aluminothermic welding // Welding International. Volume 29 - Issue 2, 2015, Pages 155-157.
[6] Kallio M., Ruuskanen P., Maki J., Poylio E., Lahteenmaki S. Use of the aluminothermic reaction in the treatment of steel industry by-products // Journal of Materials Synthesis and Processing. 2000. T. 8. № 2. С. 87-92.
[7] Yuan-qing Wang, Hui Zhou, Yong-jiu Shil, Bao-rui Feng. Mechanical properties and fracture toughness of rail steels and thermite welds at low temperature // International Journal of Minerals, Metallurgy and Materials. 2012. Vol. 19. No. 5. P. 409. DOI: 10.1007/s12613-012-0572-8
[8] Bajic D., Kuzmenko G.V., Samardžić I. Welding of rails with new technology of arc welding // Metalurgija. 2013. No. 3. P. 399-402.
[9] G.A. Dorofeev, V.A. Karev, E.V. Kuzminykh, V.I. Lad’yanov, A.N. Lubnin, A.S. Vaulin, and M.I. Mokrushin Manufacture of High Nitrogen Corrosion Resistant Steel by an Aluminothermic Method in a High Pressure Nitrogen Atmosphere Russian Metallurgy (Metally), Vol. 2013, No. 1, pp. 1–10

[10] Komarov O.N., Zhilin S.G., Predein V.V., Popov A.V. Control of the properties of metal alloys obtained by aluminothermy // IOP Conf. Series: Materials Science and Engineering 709 (2020) 033103

[11] Hossain R., Pahlevani F., Sahajwalla V. Stability of retained austenite in high carbon steel – effect of post-tempering heat treatment // Materials Characterization. 2019. Т. 149. С. 239-247.

[12] Mishra A., Maity J., Mondal C. Microstructural modifications in aisi 1080 eutectoid steel under combined cyclic heat treatment // Steel Research International. 2016. Т. 87. № 4. С. 424-435.