A new type of antifriction and wear resistant malleable cast iron

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Abstract. There is developed a technology of malleable cast iron modification on the basis of complex chemical compound of surface-active elements and their solid solutions with other elements. Silicon high content in malleable cast iron helped to develop a power efficient technology of graphitizing annealing which has considerably lower annealing temperature and complete renunciation of the second graphitizing annealing stage at the expense of its change by controlled cooling up to ferrite structure or by air cooling for perlite structure.

1. Introduction
Malleable cast iron (MCI) is a fine structural material with a wide range of mechanical, technological and service properties. Malleable cast iron wear resistance is various. Perlite MCI has good wear resistance in the conditions of lubricated friction at pressure up to 20 MPa and is worn quickly at dry friction. Perlite-ferrite MCI have comparatively bad antifriction properties in the conditions of lubricated friction and rather good ones at dry friction. However, there is a reduction of MCI cast products and their replacement with high-strength iron in recent years. The reason for MCI replacement in cast structural and antifriction materials is high power inputs fore cast graphitizing annealing. Depending on MCI chemical composition, its production technology and furnace for heat treatment, graphitizing annealing lasts: for the first stage – 3…15 h, for the second stage – 6…20 h, so the total MCI annealing lasts from 9 to 35 h.

2. Problem statement
The development of centers of crystallization that occur in super cooled melt and a modified, and, consequently, the final structure of the alloy, it is possible to control both the thermodynamic and thermo kinetic factors. Thermodynamic factors affecting the speed and density of the diffusion flow to the growing nuclei of the crystallizing substance through its thermodynamic activity. Thermo-kinetic factors affect the critical size and the rate of formation of nuclei, their number and form. As a rule, in real conditions the crystallization of the melt and the thermodynamic and thermo kinetic factors are mixed and their individual contribution to the character and type of the emerging structure of the alloy is not easy to establish.

The first task of modification is solved by introducing stabilizing (antigraphitizing) modifiers into hot cast iron, the second – by one-time or divided element introduction – graphitizers. The most interesting are the effects produced by elements of Va and VIa periodic table groups which are surface-active elements (SAE). These effects are of thermodynamic, kinetic and mixed character. Bi, Te, S, N₂, Ce, Mo, Y, B are used as stabilizing modifiers for white cast iron. Their effectiveness
reveals in extremely small amounts, especially of bismuth and tellurium: from 0.0003 % to 0.01 %. It should be stressed that Bi and Te have an advantage over other antigraphitizing elements as they do not influence annealing time if the number of nuclei does not change. At the same time, N₂, Cr, Mn or Al surplus determine the time of the annealing process themselves independently from nuclei amount.

3. Research methodology
To reduce the time of MI annealing there was developed two-stage technology of its modification on the basis of the modifier which is represented by a complex chemical compound of surface-active elements and their solid solutions with other elements. The modifier consists mainly of surface-active elements of Va and VIa periodic table groups and also aluminum, antimony, tin, copper and other elements which are added to the modifier in accordance with technological tasks. The modifier is added to iron melt in the amount of 0.005…0.01 % of hot iron mass. This amount is enough to crystallize iron according to metastable system. This so-called counter modification counteracts fading of inoculation effect during keeping iron in the ladle before filling casting molds and is based on adding small amounts of surface-active elements to typical inoculating graphitizing modifiers. Surface-active elements adsorb on the surface of graphite nuclei and prevent their premature solution in considerably overheated melt during its homogenization.

There is blocking of cast iron graphitization centers at the first stage as surface-active elements are tensioactive in hot iron relatively to the phase of nonmetallic inclusions including such clusterings as carbide-like atomic segregations, fullerenes in liquid solution of cast iron. In this method of complex melt modification antigraphitizers are elements of Va and VIa periodic table groups – Sb, Bi, S, Se, Te (their surface-active properties cause cast iron chilling); and graphitizers are C, Si, A1, Cu.

If to use classical approach, then counter modification represents combined modification of I type (formation of surface film on stimulated nuclei) and modification of II type (formation of additional stimulated nuclei).

4. Research results
Using counter modification gave the opportunity of considerable increase of carbon and silicon content in MCI (Table 1) that in its turn sharply reduced graphitizing annealing duration. There were developed two types of cast iron with average carbon content 2.9…3.3 % (in standard MCI 2.4…2.8 % C): type I, average silicon content – 1.8…3.0 % Si and type II, high silicon content – 3.0…4.0 % Si (in standard MCI 1.0…1.6 % Si). Table 1 gives some MCI compositions with reduced annealing mode and their mechanical properties.

High content of silicon in MCI according to table 1 allowed to develop a power efficient technology of graphitizing annealing. Moreover, it became possible to decrease annealing temperature by 100°C and completely renunciation the second graphitizing annealing stage changing it with controlled cooling for obtaining ferrite structure (Figure 1) or with air cooling for perlite structure (Figure 2).

Besides, controlling annealing temperature and cooling rate gives the opportunity to control the annealing graphite morphology, its distribution in matrix and quantity. High degree of graphite compactness provided rather high level of mechanical properties (Table 1). Table 2 represents time modes of MCI annealing. Researching graphitization process in MCI of a new type we found out the effect of cementite selective solution and graphitizing activity of sulfide-manganese phase (Figure 3).

Each annealing graphite inclusion has nonmetallic inclusion (Figure 3a, b). Absorption of iron-carbide fullerene complexes activating nonmetallic inclusion surfaces is represented at Figure 3c and Figure 3d, where sulfide co crystallizes with cementite and is graphitized only where perlite is. Sulfide surface inside cementite is not activated and there is no decay of complexes. The effect discovered [2] was used to increase the number of kinds of MCI of a new type with compact graphite form and to develop stable-mottled cast irons (Figure 4).
**Table 1.** MCI Chemical composition and mechanical properties.

| Iron type | Chemical composition, % to mass | Mechanical properties |
|-----------|---------------------------------|-----------------------|
|           | C   | Si  | Mn  | S   | P   | σ, MPa | δ, %  | HB, MPa |
| I         |     |     |     |     |     |        |       |         |
|           | 2.92 | 2.54 | 0.41 | 0.28 | 0.08 | 710 | 2.0 | 2300 |
|           | 3.21 | 1.74 | 0.60 | 0.28 | 0.07 | 735 | 1.8 | 2600 |
|           | 3.05 | 2.95 | 0.60 | 0.24 | 0.06 | 580 | 3.0 | 2200 |
|           | 3.28 | 2.76 | 0.44 | 0.35 | 0.10 | 550 | 2.6 | 2100 |
| II        |     |     |     |     |     |        |       |         |
|           | 2.90 | 3.55 | 0.40 | 0.33 | 0.09 | 470 | 5.5 | 2000 |
|           | 3.12 | 3.97 | 0.37 | 0.40 | 0.08 | 490 | 6.5 | 1800 |
|           | 2.92 | 3.70 | 0.33 | 0.37 | 0.09 | 610 | 2.2 | 2100 |
|           | 3.27 | 3.00 | 0.44 | 0.47 | 0.12 | 510 | 2.0 | 2000 |

**Table 2.** Modes of MCI heat treatment.

| Iron type | Optimum time of graphitizing annealing, hour |
|-----------|---------------------------------------------|
|           | For perlite* | For ferrite |
|           | 850 °C | 950 °C | 850 °C | 950 °C |
| I         | 2.0 | 0.5 | 2.0/120** | 0.5/120 |
| II        | 0.5 | 0.3 | 0.5/240 | 0.33/240 |

*Air cooling.
**The first stage of graphitization as numerator, these condstage of graphitization as denominator, replaced by cooling (V_{cool}, °C/h).

**Figure 1.** Ferrite MC Is type I, after annealing (a – 950 °C, x100; b – 850 °C, x100) within 30 min. and cooling rate 120 °C/h (nital etching)

During graphitization only outer cementite shell decays because of destabilization by endohedrals on the basis of bismuth, tellurium and copper. For this purpose we added to MCI with higher content of sulphur (0.2…0.4 %) extra chromium (up to 2.0%) to obtain stable cementite and extra copper (0.3…5.0 %) for complete perlite matrix of cast iron and further modification according to the technology of counter modification. The choice of alloying elements was based on the following:

1. Cast iron is alloyed simultaneously by graphitizing elements (Si, Cu) and antigraphitizing elements (Cr, S).
2. Cast iron alloying with copper is carried out for several reasons:
   Firstly, it is known that copper in white cast iron increases its heat conduction and most of its tribotechnical properties.
Secondly, copper in contrast to silicon destabilizes cementite because it partly enters into its composition replacing iron atoms and forming compound \((\text{Fe}_{2n}\text{Cu}_n)\text{C}\).

**Figure 2.** Perlite-ferrite MCI softype II with compact graphite form after \((a – 850 \degree \text{C}, \times 250; b – 950 \degree \text{C}, \times 250)\) within 30 min. and cooling rate 120 \degree \text{C}/h (nital etching)

**Figure 3.** Sulfide-manganese phase influence on MCI graphitization, \(\times 630\) (nital etching)

Cementite destabilizing is a direct formation of copper with fullerenes of cuprous endohedrals and bismuth and tellurium. It means that the first portions of crystallizing cementite are enriched with chromium (inner nuclei of cementite inclusions) and the last portions – with copper, which are also enriched with silicon, though with a very small amount because of its bad solubility in cementite. There is polarization of carbide phase – one of its parts becomes highly graphitized and the other (inclusion nuclei) – sharply lower.

In such cases cast iron is additionally modified by strong chilling additives of bismuth and tellurium bismuth and tellurium. Adding chromium into cast iron (about 2 \%) sharply stabilized cementite structure of cast iron (Figure 4a). Total perlite structure was obtained only after 3 h at heating up to 1000\degree \text{C}, and 8 h were needed for decay of ledeburite frames on isolated cementite inclusions (Figure 4a, b).

The experimental results also showed that there was intensive release of annealing graphite on sulphide phase (Figure 4c). In general, the structure obtained is a composite one: evenly distributed
isolated cementite inclusions in perlite matrix. Tribotechnical tests were carried out according to the standard technique on friction machine SMC-2 using counter face made of hard steel 40X at block pressure to the roller 120MPa in distilled water simulating the conditions of half-floating condition. Table 3 represents data on the wear of stable-mottled cast irons.

Table 3. Chemical Composition, Tribotechnical and Mechanical of Stable-mottled Cast Irons.

| Chemical composition, % to mass | Wear, mg/(cm²km) | Friction coefficient | σB, MPa | HB, MPa |
|--------------------------------|------------------|----------------------|---------|---------|
| C   | Si   | S   | Cu   |                  |       |         |         |         |
| 2.80 | 4.40 | 0.92 | Сл. | 7.0 | 0.10 | 280 | 2010 |
| 3.23 | 3.40 | 1.11 | Сл. | 5.8 | 0.09 | 292 | 2210 |
| 3.60 | 2.40 | 1.39 | Сл. | 4.4 | 0.07 | 271 | 2100 |
| 1.80 | 4.40 | 0.92 | 4.99 | 6.7 | 0.09 | 490 | 2400 |
| 2.22 | 3.41 | 1.11 | 3.02 | 5.4 | 0.07 | 382 | 2260 |
| 3.56 | 2.41 | 1.37 | 0.30 | 4.3 | 0.07 | 245 | 2210 |
| 2.82 | 4.36 | 0.92 | 0.33 | 8.2 | 0.11 | 492 | 2100 |
| 2.17 | 3.37 | 1.12 | 3.22 | 6.1 | 0.10 | 390 | 2010 |
| 1.85 | 2.41 | 1.40 | 4.96 | 6.6 | 0.08 | 578 | 1970 |

Note: Cr up to 2.0%; Mn up to 0.4%; P up to 0.3%

5. Conclusion
On the basis of cast iron counter modification there was developed a new group of constructional cast irons having unique technological, functional, mechanical and service properties, first of all antifriction and wear resistant. This group includes cast irons with reduced annealing mode, their structure being controlled by annealing temperature or cooling rate during graphitization; high-strength cast irons with compact graphite form and stable-mottled cast irons with controlled amount of graphite and carbide phase.

6. References
[1]. Zhukov A A and Davydov S V 1983 Malleable cast iron with short mode graphitizing annealing Steel in Translation 6 pp 100-103
[2]. Zhukov A A and Davydov S V 1983 On the graphitizing effect of sulphide inclusions in stable-half the iron Met Sci Heat Treat. 4 pp 36-37