

Modification and Microalloying of Iron Carbon Alloys Using Industrial Polymer Scrapes

Aliaxandr I. Harast

Department of Metals and Materials, Belarusian State University of Technology (BSTU)

13a, Sverdlova str., 220050, Minsk, Republic of Belarus

garost-51@tut.by

Abstract- The information about highly effective stimulation methods of modification and microalloying in the formation of iron-carbon alloys structure is presented. The effect of additives in minor quantities is implemented by refining effects, and by influencing the structure and composition of the liquid and solid phases, the morphology and composition of nonmetallic inclusions, intermetallides, borides, nitrides, crystallization conditions, the size and boundaries of the primary and secondary crystal grains. The developed method of finishing iron carbon alloys allows recycling carbon-containing products from organic high molecular weight polymer materials of synthetic origin, including biologically damaged, aged, and unfit for recycling materials from plastics and elastomers unsuitable for regeneration. Cheap modifying additives for cast iron were developed. The introduction of these additives significantly improves the structure and mechanical properties of alloys.

Keywords – Industrial Polymer Scrapes; High Molecular Weight Compounds; Iron-carbon Alloys; Baling; Modification; Alloying; Carbonizing; Structure Formation; Microcomposition and Morphology of non-Metallic Inclusions

I. INTRODUCTION

Further improvement of the quality of steel and cast iron is limited by the characteristics of the existing modifiers and it can only be obtained by employing non-classical methods of treatment of melts. The materials providing the maximum effect may be incapable for regeneration high polymeric compounds, in which carbon can be either chemically bound or free in the structural state [1–2]. The use of polymeric materials of synthetic origin as additives, including biologically damaged, aged, and unsuitable for the processing materials from plastics, as well as unsuitable for regeneration elastomers which form atomic hydrogen and carbon (H^+ , C^{4+}) in the melt during pyrolysis, provides the refining effect and the effective impact on the composition and structure of the liquid and solid phases, the morphology and composition of non-metallic inclusions, intermetallides, borides, nitrides, crystallization conditions, the size and boundaries of the primary and secondary crystal grains [8 – 12].

In particular, the worn industrial rubber products can be regarded as secondary raw materials [1, 5]. Their processing could save a large amount of expensive and scarce materials, which is of great economic importance.

It is unpractical to regenerate industrial rubber products which contain a high percentage of textile, and little of rubber. Each tire contains 26 per cent of carbon, 12.5 per cent of metal, and over 50 per cent of rubber [3].

Elastomers may be a promising additive in smelting ferrous metals (steel and cast iron) and an effective substitute for expensive alloying and scarifying additives. Introduction of such compounds in the melt provides refining, modifying, and microalloying effects [3].

High polymer compounds being added to the melt can provide a modifying effect in two ways [1]. At the first stage in the process of pyrolysis of rubber it is due to the formation of ions C^{4+} , and at the second stage when structurally free carbon in the form of black carbon and other elements of the additives (Cu, Ti, Al, Co, Pb) are activated.

More electronegative than iron (e.g. Ca) metals substitute carbon in cementite, reduce resistance of carbide and promote graphitization. Such elements as Al, Si, P, and S to some extent, being dissolved in the iron as Al^{3+} , Si^{4+} , P^{5+} , S^{6+} ions having external P^{σ} - shells stabilize the body-centered cubic forms α -, δ - solutions and melts with the same short-range order. They displace carbon (C^{4+}) from the solution, increasing its reactivity and promoting graphitization [3, 4, 6]. The composition of high molecular weight polymer compounds (Table III) comprises a number of other elements (Cu, Ti, Al, Ni). In most cases, the modifying effect of a particular element is much stronger than the actual alloying, and the nature of such effects remains unclear [7].

II. INVESTIGATION OF INTRODUCTION METHODS INTO THE MELT AND THE PERSPECTIVES OF USING HIGH MOLECULAR WEIGHT POLYMER COMPOUNDS AS ADDITIVES IN ALLOYING AND MODIFYING IRON CARBON ALLOYS

In the Belarusian State University of Technology a method of smelting cast iron and a method of steel smelting were developed [3]. In these techniques the elastomers or biologically damaged or aged plastics bound into scrap bales isolated from

the air are introduced into in the melt as additives.

When this technology is implemented, the following high molecular weight industrial wastes are processed [3].

Plastics – polyolefins, aliphatic polyamides, which do not tend to coke formation during thermal degradation; polyphenylenes, polyamides, polybenzimidazoles which tend to form coke;

Elastomers – silicone rubber, acrylic rubber, ethylene propylene rubber, polychloroprene rubber, polysulfide rubber, butyl rubber, polyurethane, and rubber products containing cord and wire.

To study the influence of rubber products as additives on the characteristics of iron carbon alloys (such as gray iron), and to investigate the methods of introduction wastes of polymer compounds into the metal melts vehicle tires for trucks were used.

Table I presents the results of the melts of gray cast iron in the induction furnace IST-04. The introduction of rubber-containing wastes pressed in metallic glasses in the form of strips bound into bunches was investigated. The dissolution of the constituent blocks occurred quite slowly (~ 10 min.) as they were warmed up. Steel glasses with waste elastomers were fed into the crucible furnace at the finishing stage of the melt.

TABLE I CHARGE COMPOSITION AND THE METHOD OF MODIFYING CAST IRON IN THE EXPERIMENTAL INDUSTRIAL MELTS

№ of the melt	Charge composition	Modification method
1	Pig-iron 7kg ×16 units= 112 kg Chemical boring 12 kg Grab Iron ~276 kg	Original composition, modification was not carried out
2	-----	The melt was modified by 1.43 % of rubber
3	Total ~400 kg	The melt was modified by 4.28 % of rubber

The chemical composition of cast iron was determined on the "Spektrolab - 5M" (Table II).

Peculiarities of the behavior of the modifying agent (rubber waste) are presented in Table III. The degree of carbon recovery modifier ranges from 25 - 32%.

TABLE II THE CHEMICAL COMPOSITION OF THE SAMPLES OF CAST IRON OF INDUSTRIAL MELTS (DEFINED ON THE "SPEKTROLAB - 5M")

Modification method	Component composition, % wt													
	C	Si	Mn	P	S	Mg	Cr	Ni	Mo	Cu	Al	Ti	V	Nb
Original composition, modification was not carried out	3,32	2,00	0,543	0,081	0,06	<0,001	0,11	0,055	0,003	0,11	<0,001	0,021	0,010	<0,001
The melt was modified by 1.43 % of rubber	3,35	1,95	0,546	0,081	0,059	<0,001	0,11	0,055	0,003	0,11	<0,001	0,020	0,010	<0,001
The melt was modified by 4.28 % of rubber	3,40	1,95	0,546	0,075	0,065	<0,001	0,11	0,054	0,002	0,11	<0,001	0,019	0,010	<0,001

TABLE II (CONTINUE)

Modification method	Component composition, % wt												
	W	Co	Zr	B	Ca	Sb	As	Sn	Pb	Zn	Bi	Se	
Original composition, modification was not carried out	<0,005	0,004	<0,001	0,0008	<0,0001	<0,001	0,005	0,002	<0,001	0,010	<0,001	<0,001	
The melt was modified by 1.43 % of rubber	<0,005	0,004	<0,001	0,0008	<0,0001	<0,001	0,005	0,002	<0,001	0,009	<0,001	<0,001	
The melt was modified by 4.28 % of rubber	<0,005	0,004	<0,001	0,0009	<0,0001	<0,001	0,005	0,002	<0,001	0,009	<0,001	<0,001	

TABLE III THE COMPOSITION OF THE MODIFYING AGENT (RUBBER WASTE) AND THE DEGREE OF CARBON RECOVERY

Modification method	The estimated chemical composition of the modifier, % wt	The weight of the introduced modifier (rubber), kg	Carbon weight in the composition of the modifier, kg	The degree of carbon recovery from modifier (for 400 kg of the melt), %
Original composition, modification was not carried out	C (chemically bound)– 35,70; C (as black rubber)– 30,77; C (total introduction) – 66,47;	-	-	-
The melt was modified by 1.43 % of rubber	H ₂ – 17,17; S – 1,50; Zn – 1,59;	0,570	0,38	31,6
The melt was modified by 4.28 % of rubber	Cu, Ti, Al, Fe, Ni – minor amounts	1,710	1,14	28,1

III. MECHANICAL CHARACTERISTICS OF THE RESULTED ALLOYS

The results of the investigations of the mechanical characteristics (TABLE IV) indicate the effectiveness of modification of cast iron by polymer compounds (e.g. rubber waste). The rupture strength increases from 177.0 MPa (original cast iron) to 192.0 MPa (when modified by 1.71 kg of rubber). Modification results in cast iron trademark 'CG 20'.

TABLE IV MECHANICAL CHARACTERISTICS OF THE SAMPLES OF CAST IRON OF INDUSTRIAL MELTS

Modification method	Rupture strength, σ , MPa	Hardness HB, MPa
Original composition, modification was not carried out	177,0	1790
The melt was modified by 4.28 % of rubber	192,0	1970

IV. METALLOGRAPHIC EXAMINATION OF THE OBTAINED ALLOYS

The structure of the resulting iron was investigated in accordance with the national state standard GOST 3443-87. When graphite is evaluated, the form, distribution, size and number of inclusions are considered. When the metal base is evaluated, the type of structure, the form of pearlite, the amount of pearlite and ferrite, the pearlite dispersion are considered.

The study of graphite was carried out on non-etched specimen, and the metal base – on specimen after etching (Fig. 1-4). To etch the surface of the specimen the reagent of the following composition was used: 4 ml of HNO₃ (density is 1.4 g/cm³), and 96 ml of ethyl alcohol.

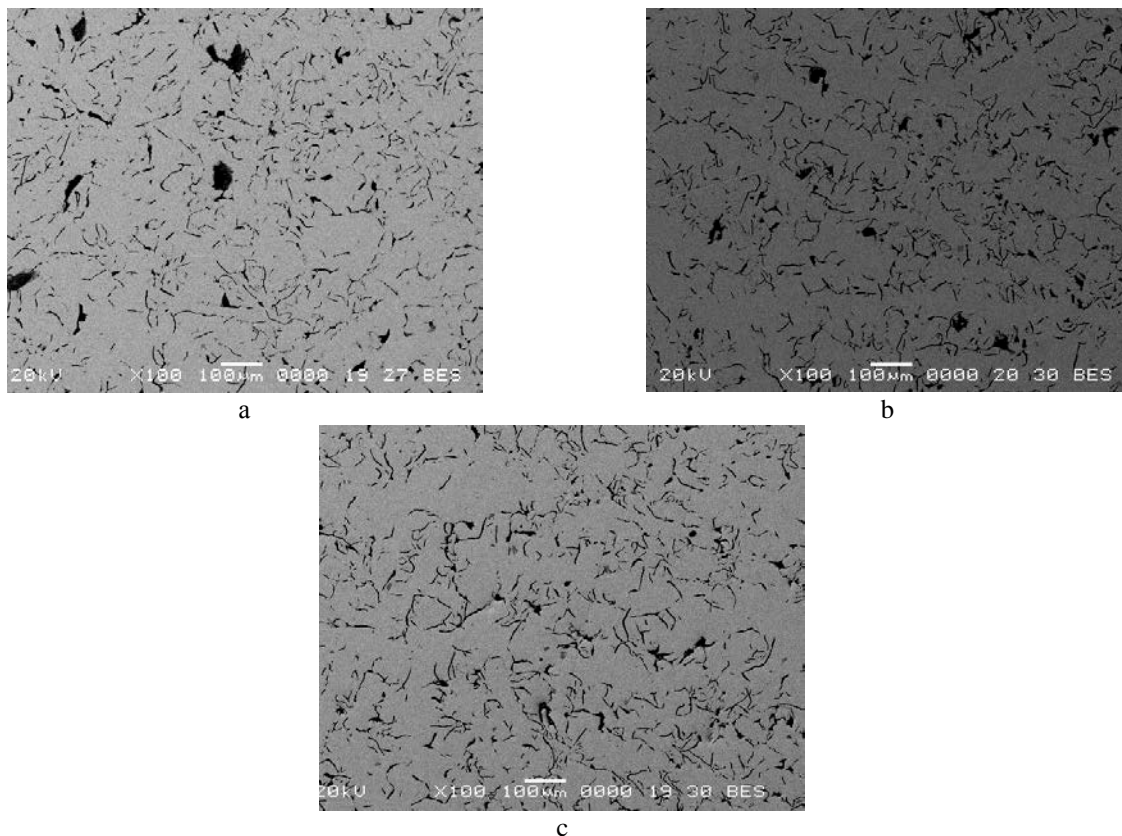


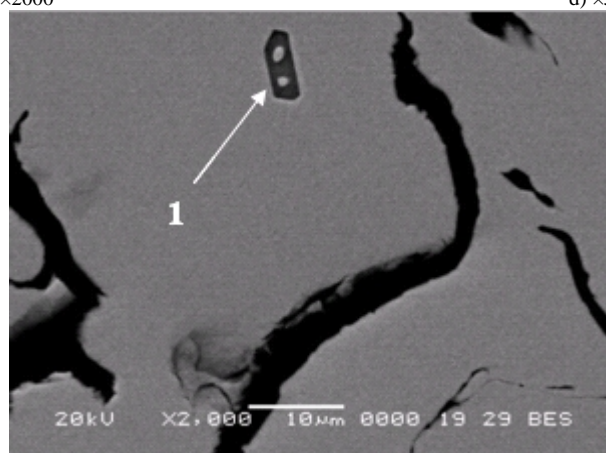
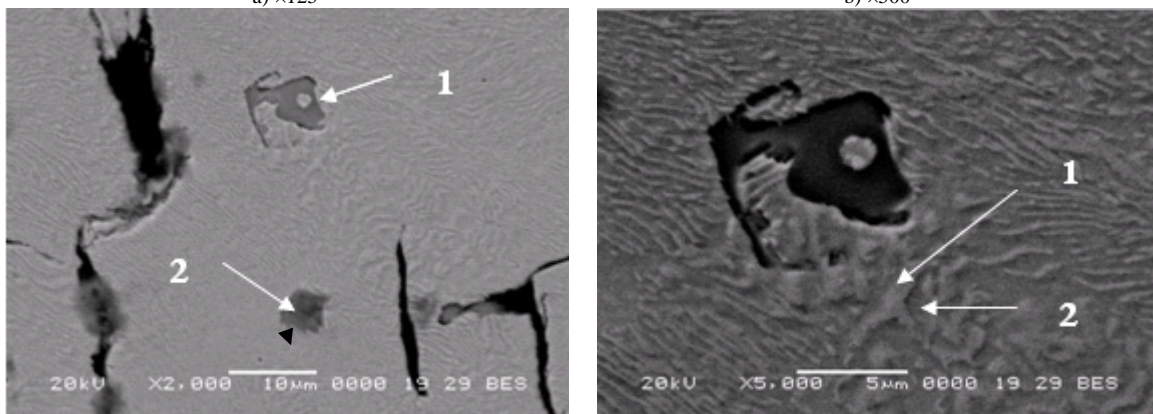
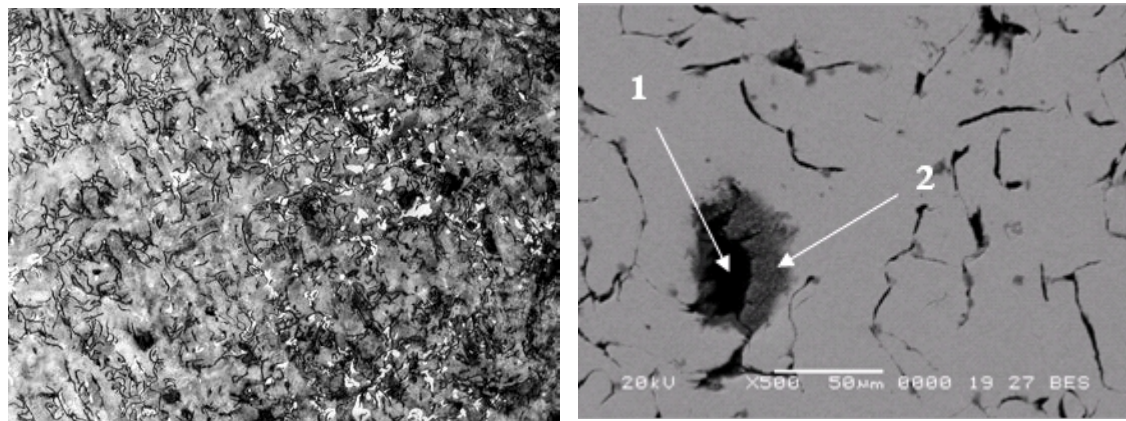
Fig. 1. Microstructure ($\times 100$) of cast iron of industrial melts (investigations by scanning electron microscopy): a – original composition,

(modification was not carried out); b – the melt was modified by 1.43 % of rubber; c – the melt was modified by 4.28 % of rubber.

To determine the structure of cast iron the sections were viewed under the microscope with the following power:

- (a) an overview of the structure – at 10 to 200 times power;
- (b) to define the form, the principle of distribution, size and number of graphite inclusions – at 100 times power;
- (c) the type of metallic base – at 500 times power;
- (d) the amount of pearlite and ferrite – at 100 times power;
- (e) the dispersion of lamellar pearlite – at 500 times power.

The structure of cast iron was analyzed in accordance with the national state standard 3443-87 comparing visually the structure that is visible in the microscope and the structure of an appropriate scale (Table V).



e) ×2000

Fig. 2. Microstructure of cast iron (etched specimen) of the original composition (modification was not carried out): a – metallographic investigations; b, c, d, e – investigations by scanning electron microscopy.

The microstructure of the original cast is non-uniform (Fig. 1a, 2). A significant amount of interdendritic spotted graphite of quite a large size is observed, but there is also precipitation of flake graphite mainly of vortex shape. Pearlite is lamellar, sorbitic.

Ferrite clustering is observed where there are graphite inclusions. Along the grain boundaries the inclusions of phosphide eutectic can be detected.

Modification of cast iron by high molecular weight polymer compounds (rubber wastes) improves cast iron structure.

TABLE V CHARACTERISTICS OF THE COMPONENT STRUCTURE ACCORDING TO THE NATIONAL STATE STANDARD –‘GOST3443-87’

Modification method	Component structure	The estimated parameter	Symbolic Notation
Original composition, modification was not carried out	Graphite PG	Shape of inclusions Size of inclusions Distribution of inclusions Amount of inclusions	PGf2 PGd45 (30-60 μm) PGr1, PGr6 PG10 – PG6
	Pearlite PT1	Degree of fineness Grade of Concentration	PD 0,3 – PD 0,5 P85
	Phosphide eutectic	Structure of inclusions Area of inclusions	Triple fine-grained F3 Triple acicular F4 Fp<2000
The melt was modified by 1.43 % of rubber	Graphite PG	Shape of inclusions Size of inclusions Distribution of inclusions Amount of inclusions	PGf2 PGd25 - PGd45 (15-60 μm) PGr1, PGr6 PG6 – PG4
	Pearlite PT1	Degree of fineness Grade of Concentration	PD 0,5 – PD 1 P92 – P96
	Phosphide eutectic	Structure of inclusions Area of inclusions	Triple fine-grained F3 Fp<2000
The melt was modified by 4.28 % of rubber	Graphite PG	Shape of inclusions Size of inclusions Distribution of inclusions Amount of inclusions	PGf2 PGd45 (30-60 μm) PGR1, PGR6 PG6
	Pearlite PT1	Degree of fineness Grade of Concentration	PD 0,5 – PD1 P96
	Phosphide eutectic	Structure of inclusions Area of inclusions	Triple fine-grained F3 Fp<2000

- The size of significant graphite precipitation reduces, and when the amount of introduced modifying agent is increased up to 4.28%, such inclusions are virtually absent (Fig. 1c).

- The amount of pearlite component in the ferrite - pearlite metal base of the considered gray cast iron is increased from 85% (original composition, modification was not carried out) to 92 - 96% (melts 2 and 3) after introducing the wastes of high molecular weight polymer compounds, i. e. from P85 (Fe15) to P96 (Fe4).

V. ELECTRON MICROSCOPIC STUDY OF THE RESULTED ALLOYS

Under normal magnification (Fig. 1-4) pearlite lamellar structure of the metal base is not clearly differentiated, it required investigating with SEM microscope JSM-5610LV (firm IEOL, Japan) with a system of electron - probe energy dispersive X-ray analysis. Alloy structure was fixed with secondary electron detector (Fig. 2-4).

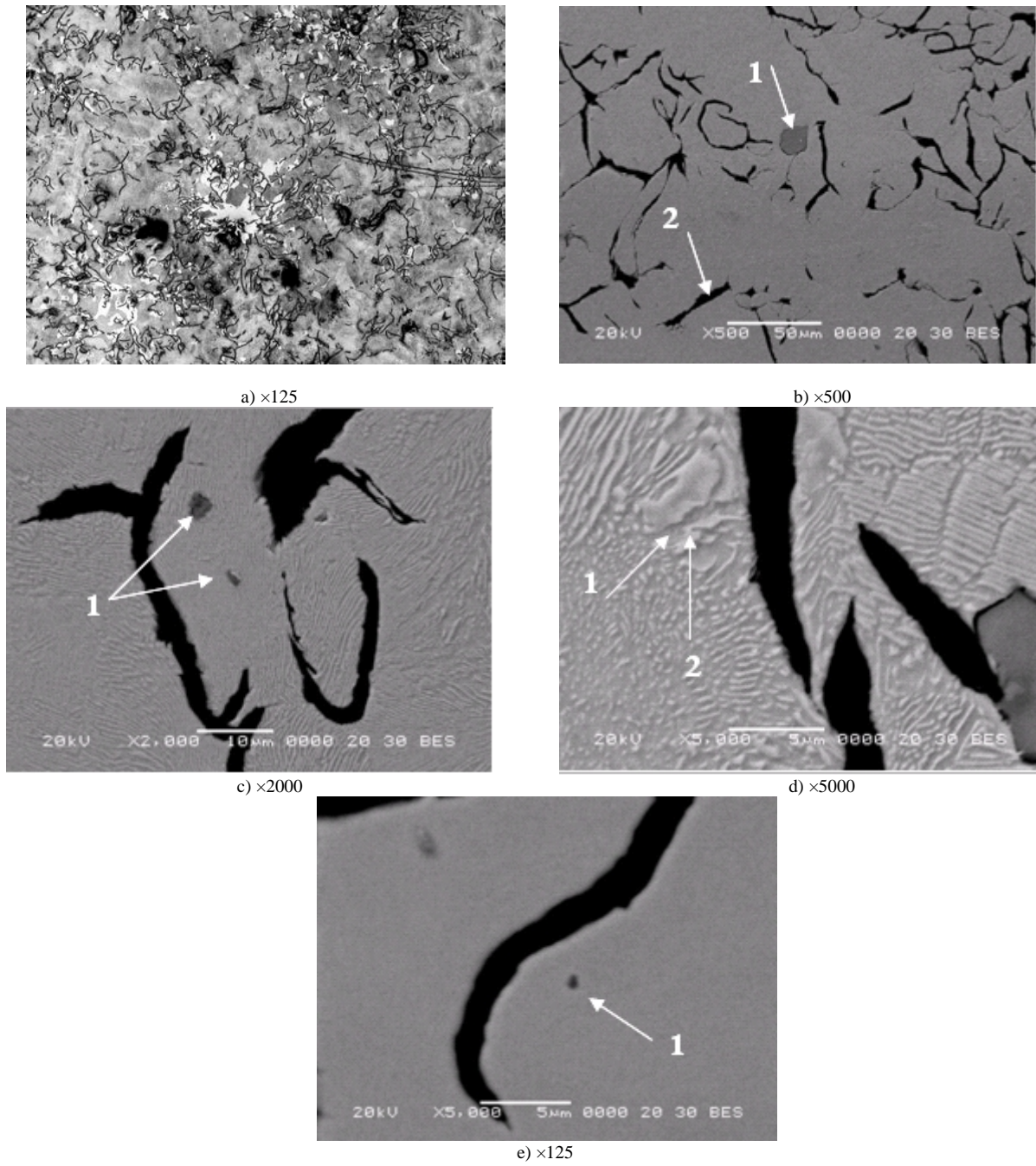
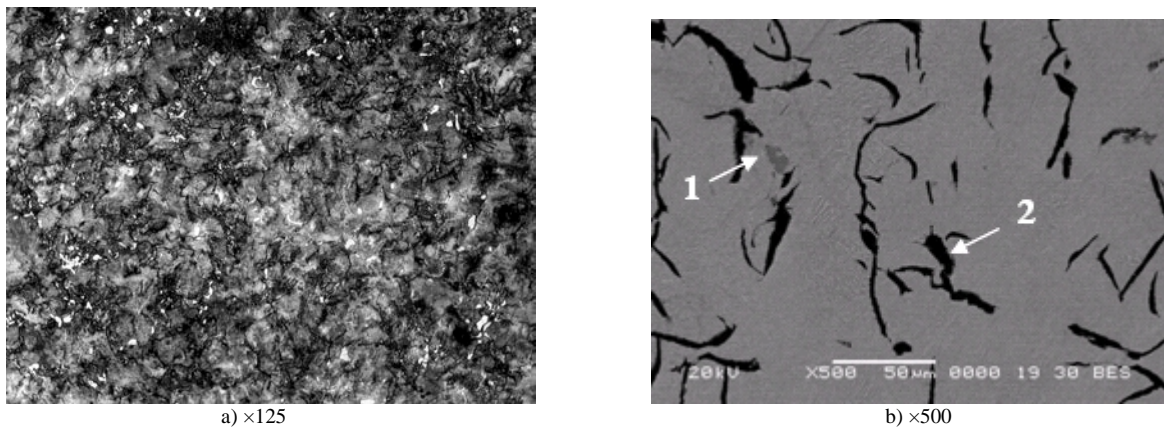


Fig.3. Microstructure of cast iron (etched specimen) of the melt modified by 1.43 % of rubber: a – metallographic investigations; b, c, d, e – investigations by scanning electron microscopy.



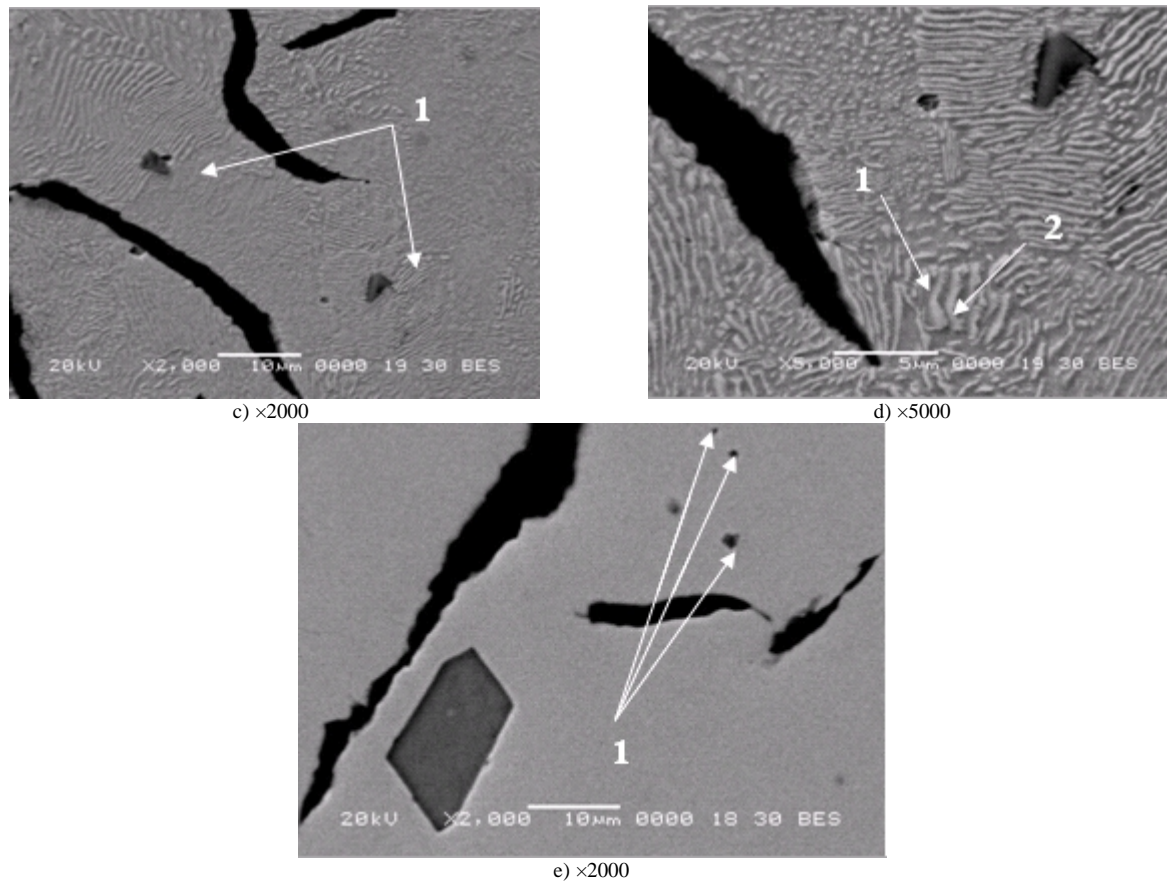


Fig. 4. Microstructure of cast iron (etched specimen) of the melt modified by 4.28 % of rubber): a – metallographic investigations; b, c, d, e – investigations by scanning electron microscopy.

In the study of the original and modified cast iron specimen by scanning electron microscope the composition (Table VI) and morphology of the resulting chemical associations (non-metallic inclusions and other "secondary" phases) were determined.

In the original cast iron graphite precipitated as lamellar structure mainly of vortex shape and there is interdendritic spotted graphite of quite a large size

(Fig. 1a, 2). Thus on graphite inclusions (pos. 1 Fig. 2b) there are deposited iron and chromium oxides and possibly chromium carbides (pos. 2 fig. 2b). Such complex precipitations have little relation to the matrix and adversely affect the properties of cast iron. Manganese sulphides (pos.1 Fig. 2c) have a branched form (the same inclusions in a larger scale are shown in (Fig. 2d)). There are also more compact sulfides (pos. 1 Fig. 2e).

Inclusions of titanium nitrides (pos. 2 Fig. 2c) have a diameter size of about 3 μm , while in the composition of these inclusions the complex oxide component is present in small quantities.

In the cast iron modified by 1.43 % high molecular weight compound (Table VI) the inclusions of the interdendritic spotted graphite are much smaller, with no graphite inclusions on the precipitated oxides (pos. 2 Fig. 3b), but some amount of oxygen is likely to precipitate in the graphite without formation of compounds. Manganese sulphides have a compact form (pos. 1 Fig. 3b). Inclusions of titanium nitrides (carbonitrides) (pos.1 Fig. 3c) of a smaller diameter (maximum 2 μm) than those of the original cast iron comprise a minor quantity of a sulfide component. There are also titanium nitrides (pos.1 Fig. 3d) without any sulfide component. Ferrite plates (pos.2 Fig.3d) and cementite plates (pos. 1 fig.3d) in the pearlite component differ only in the concentration of carbon.

In the cast iron modified by 4.28 % high molecular weight compound (Table VI) the lamellar graphite inclusions (pos.2 fig. 4b) of vortex shapes contain dissolved oxygen; there are no significant precipitation of spotted interdendritic graphite. Manganese sulphides, like in the introduction of 1.43 % polymer compound, have a compact form (pos.1 Fig. 4b). The inclusions of titanium carbide (pos.1 Fig.4c) and titanium nitride (pos.1 Fig.4d) can be clearly differentiated, and such inclusions have a dispersive structure (the size is not more than 1 - 2 μm). Such particles formed in the molten cast iron are likely to become the nucleating seeds. As in the case of the introduction of 1.43 % polymer compound the ferrite plates (pos.1 Fig.4d) and cementite plates (pos.2 Fig.4d) in the pearlite component differ only in the concentration of carbon.

The above described investigations indicate the effectiveness of the introduction of the waste high-molecular weight polymer compounds (e. g. used tires) in the cast iron. The result of successfully solved problems is utilization of waste rubber products, as well as a significant increase in quality of cast iron.

TABLE VI THE CHEMICAL COMPOSITION OF NONMETALLIC INCLUSIONS OF THE INVESTIGATED CAST IRON MELTS

Modification method	Position of the inclusions	Component composition, % wt													
		C	O	Si	P	S	Al	Mn	Cr	Ni	Ti	Cu	Ca	N	Fe
Original composition, modification was not carried out	1(fig.2b)	100,0	-	-	-	-	-	-	-	-	-	-	-	-	-
	2(fig.2b)	23,14	28,70	0,93	0,05	1,18	0,36	0,18	12,48	0,06	0,08	-	0,66	-	32,18
	1(fig.2c)	11,35	-	0,33	-	30,77	-	45,92	0,32	-	-	-	0,22	-	11,09
	2(fig.2c)	6,99	6,24	0,11	0,24	0,07	-	0,59	2,47	-	51,68	0,44	-	14,87	16,31
	1(fig.2e)	29,74	1,72	0,08	-	20,19	-	42,12	0,14	-	-	0,21	0,02	-	5,79
The melt was modified by 1.43 % of rubber	1(fig.3b)	18,35	0,39	0,05	-	27,38	-	51,71	0,25	-	-	-	0,03	-	0,20
	2(fig.3b)	73,96	14,07	0,18	0,03	-	0,03	0,14	-	-	0,07	-	0,04	-	11,46
	1(fig.3c)	13,50	1,08	0,51	-	3,23	-	5,01	2,10	0,04	48,59	0,36	-	6,24	19,33
	1(fig.3d)	12,81	-	1,06	-	-	-	0,50	0,24	-	0,16	-	0,16	-	85,06
	2(fig.3d)	5,83	0,79	1,12	-	-	-	0,82	0,22	1,14	0,17	0,01	0,25	-	89,65
	1(fig.3e)	7,37	2,23	0,82	-	0,21	-	0,78	0,54	0,21	12,65	0,15	-	6,77	68,26
The melt was modified by 4.28 % of rubber	1(fig.4b)	8,83	3,29	0,33	-	29,73	-	55,77	0,02	-	0,29	-	0,35	-	1,39
	2(fig.4b)	38,23	25,88	0,80	-	0,11	-	0,47	0,31	-	0,17	-	0,12	-	33,91
	1(fig.4c)	8,97	-	0,74	-	0,56	-	-	3,39	0,46	72,52	0,09	-	-	13,27
	1(fig.4d)	12,25	-	1,78	-	0,09	0,11	-	0,31	0,55	0,17	0,42	-	-	84,34
	2(fig.4d)	16,00	-	1,43	0,10	0,02	-	0,52	0,26	0,44	0,01	0,10	0,02	-	81,11
	1(fig.4e)	8,93	0,20	0,46	0,02	2,19	-	3,76	2,35	-	32,50	-	-	5,79	43,79

VI. CONCLUSIONS

The developed method of finishing iron carbon alloys allows recycling carbon- containing products from organic high molecular weight polymer materials of synthetic origin, including biologically damaged, aged, and unfit for recycling materials from plastics and elastomers unsuitable for regeneration. Cheap modifying additives for cast iron were developed. The introduction of these additives significantly improves the structure and mechanical properties of alloys.

Implementation of the method can effectively saturate the iron-carbon alloys with carbon instead of the traditional method of dilution; it allows obtaining carbon of high quality from the waste high molecular weight polymer compounds; it allows extracting expensive and scarce metals from oxides and introducing them effectively into the melts; it allows recycling industrial scales and rubber wastes.

The process of formation of nonmetallic inclusions in the iron-carbon alloys is studied and scientifically grounded; the microcomposition and morphology of the formed chemical associations are investigated. New scientific information is presented about the peculiarities of structure and properties of iron-carbon alloys, the principles of the additives distribution within the phases, both core and some trace elements, either accidentally or deliberately introduced into the melt in the process of deoxidation, modification, or microalloying in the microcomposition and non-metallic inclusions.

REFERENCES

- [1] Harast A. I. Iron Carbon Alloys: Structure Formation and Its Properties. Minsk , 2010.- 252p.
- [2] Harast A.I. "Physics and Chemistry of the Technology of Alloying, Modifying, and Hardening of Iron Carbon Alloys with Industrial Wastes and Semifinished Products of the Related Industries." Research Notes. Lutsk National Technical University.- 2013, vol. 43. – pp. 46-51.
- [3] Patent 116411 of the Republic of Belarus "Method of Cast Iron Smelting and Method of Steel Smelting" (2006) C 21 C 1/00, C 21 C 5/00, F 23 G 5027 / Harast A.I. BSTU – № a20050280; appl. 24.03.2005; publ. 30.12.2006 // The Official Journal. – 2009 . – № 1.
- [4] Goldstain Y.E., Misin V.G. "Cast Iron and Steel Modifying and Microalloying.", Metallurgy.1986.
- [5] Harast Aliaxandr Ivanavich. Chemical Baling of Oily Cast Iron Turnings and Use of Bales to Substitute Expensive and Scarce Scrapes. *International Journal of Materials Science and Applications*. vol. 2, No.6, 2013, pp. 194-203. doi: 10.11648/j.ijmsa.20130206.15
- [6] Grigorovich V.K. "Thermodynamics, Physical Kinetics of Structure Formation and Properties of Cast Iron and Steel." ed. 4, 1971, pp. 36-47.
- [7] Girshovich N.G. Ioffe A. Y., Zommer L. R "Thermodynamics, Physical Kinetics of Structure Formation and Properties of Cast Iron and Steel." ed. 4, 1971, pp. 380-383.
- [8] Shulte Y. A. "Electrometallurgy." Metallurgy; 1970, p.223.
- [9] Kreshchanovsky N. S., Sydorenko M. Ph. "Steel Modifying." Metallurgy, 1970, p.296.
- [10] Harast A.I. "Structure Formation Mechanism in Alloyed Wear-resisting Cast Iron." Casting and Metallurgy, 2012, № 3. – pp. 101-113.

- [11] Goretsky G. P., Vajsová V. V., Pavlovich V. G. "Improvement of Structure and Properties of Fe-C-alloys in Direct Doping." *Metallurgy Engineering*. – 2011, № 3. – pp. 15-18.
- [12] Harast A. I. "Utilization of Metal-containing Wastes to Strengthen Machine Parts from Nano- to Macrolevel." *Equipment Stock*. – 2011, №5 (82). – pp. 85-87.



Harast Aliaxandr Ivanavich was born in the Republic of Belarus, Brest Region, in 1951. He is Associate Professor of the Department of Metals and Materials of the Belarusian State University of Technology. He is Philosophy Doctor in Engineering Sciences.

The author has more than 210 scientific and technical publications, 40 inventor's certificates, and 12 patents of the industrially developed countries (the USA, Germany, Italy, Japan, Great Britain, Sweden, Finland, and India).

Dr. Harast worked out recourse-saving import-substituting technologies in metallurgy which provide recycling industrial wastes and by-products of relating industries. The method of direct volume alloying of iron-carbon alloys and direct surface alloying of cast section is implemented. He worked out oil-free coolant, composition and treatment schedule, processing techniques of special types of steel and cast iron, mass exchange regulation methods in metallurgical units by external electric fields, environmentally friendly technology of chemical baling of oily cast iron turnings. The results of investigations are efficiently employed in different plants and enterprises of the Republic of Belarus.