

# The Casting Technologies Focused on the Use of Industrial Waste and Semiprocessed Products Related to Engineering Industries

Harast A. I.

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

**Abstract**—The important direction in the economy of the metals used in the composition of the alloying and modifying additives in the alloy smelting is extraction of metals from waste and semiprocessed products of related industries. When implementing technology, the non-conventional metallurgical materials are used as reducing agents, namely, carbon-containing organic high molecular weight polymeric materials (HMWPM) of synthetic origin, including biologically damaged and subjected to ageing and unsuitable for processing plastics materials as well as unsuitable for reduction elastomers. New scientific information is obtained about the peculiarities of structure formation on the example of the titanium alloy modification from industrial waste and the properties of alloys, including the distribution between the phases of both core elements, and other additives, accidentally or deliberately introduced into the melt in the process of deoxidation, modification, or microalloying in the microcomposition and nature of non-metallic inclusions.

**Keywords**—iron-carbon alloys, cast iron, alloying, modification, titanium-containing industrial waste, man-made waste from high molecular weight compounds, structure formation, microcomposition, and morphology of non-metallic inclusions.

## I. INTRODUCTION

The important direction in the economy of the metals used in the composition of the alloying and the modifying additives is extraction of metals from the waste and semiprocessed products of related industries.

In this regard, non-classical resource-saving metallurgical technologies involve the use and recycling of industrial waste and semiprocessed products related to engineering industries at all stages of the metallurgical treatment [1 - 3]:

- when melting in the blend of metal oxides, scale, grinding waste, oily cast iron turnings, and non-regenerated by conventional methods highly polymeric compounds in which carbon is in a chemically bound state, and a structurally free state;

- at the final stage of the melt by the methods of direct alloying and modification, including direct surface alloying and modification in the mold when the products of pyrolysis which can not be regenerated

from high molecular weight compounds are used as reducing agents;

- at the stage of thermal treatment of products made of ferrous metals as a cooling medium of a new product, which is the aqueous solution of the optimal concentration of the neutralized product of the alkaline hydrolysis of polyacrylonitrile polymer which does not produce smoke, soot, oil vapors, products of oxidation and thermal decomposition of hydrocarbons.

Technical and patent sources [1, 4, 6], as well as the industrial production experience suggest using the most promising methods from the point of view of new components of metallurgical raw materials that are mostly in the form of oxides (scale, rust, grinding scrapes, wastes of facing materials and so on).

The worked out catalysts of chemical, petrochemical, and production of fertilizers industries which can be used when modifying and microalloying cast iron can be referred to these wastes; they contain  $Al_2O_3$ ,  $SiO_2$ ,  $CaO$  as well as the oxides of nickel, molybdenum, cobalt, copper, chromium and tungsten in amounts from 2-10% to 50%. Significant amounts of oxides (oxides of titanium, zirconium and others) are used in glass industry as raw materials.

The idea of implementing the alloying technology at the slag phase [4] in the iron-carbon alloys production is not widespread due to the lack of effective reducing agents, and the lack of reactivity of carbon and silicon to a number of oxides; besides, the degree of the alloying elements recovery from the slag is controlled by the reaction of the alloying elements with iron oxides. It requires the creation of non-traditional molten mass processing methods which provide the efficient processing of materials containing elements with a higher affinity to oxygen.

The use of strong reducing agents such as atomic hydrogen and carbon can solve the problem by replacing the costly alloys when alloying and modifying alloys by implementing the technology of direct alloying at a new level. The materials capable of providing the maximum effect can be the high molecular weight polymer compounds unsuitable for regeneration, in which the carbon is in a chemically bound and structurally free state [1, 2, 7, 8, 9]. Metals can be efficiently reduced by alloying and modifying additives of metal-containing chemical compounds together with the carbon-containing organic high molecular weight polymeric materials of synthetic origin, including biologically damaged and subjected to ageing and unsuitable for processing materials of plastics, and also unsuitable for regeneration elastomers, which form in the melt atomic hydrogen and carbon under pyrolysis.

Thus, when implementing the technology of doping and modification of iron-carbon alloys the following high-molecular industrial waste products as reducing agents are processed.

Polyolefins which are not prone to the coke formation of during thermal degradation, aliphatic polyamides or polyphenylenes liable to coke formation, polyamides, polybenzimidazoles are obtained from plastics.

Silicone, acrylic rubbers, ethylene-propylene, chloroprene, polysulfide based rubbers, butyl rubbers, polyurethanes, and cord- wire-containing rubber products are obtained from elastomers.

In this case, the melting of industrial waste and the reduction of metals by synchronizing the melting of the starting components of the reaction (metal oxides, including industrial scale, and grinding waste) and the reduction process in the volume of the melt products of pyrolysis of organic materials should be carried out with strict technological methods using materials in bales at a specified faction.

## II. RESOURCE-SAVING TECHNOLOGY OF HARDENING OF ALLOYS

The use of titanium in cast iron is promising [5]. Titanium influences most effectively on the properties of cast iron when relatively small amounts (from 0.1 to 0.4%, and even less) are added. It is established that titanium content within these limits in the cast iron has a graphitizing action. However, titanium additive grinds graphite and contributes to its more uniform distribution. In this respect, titanium is much stronger than other alloying elements. Graphite is obtained in the shape of thin plates or in the shape of a little vortex of a pseudoeutectic type.

The graphite shape obtained in the titanium cast irons can be explained by deoxidizing titanium action. The resulting titanium oxide can be the base for the graphite formation. Such titanium action naturally contributes to increasing cast iron resistance at high temperature [5].

The most efficient way of the titanium introduction in the melt is the direct doping of oxides. In the presence of effective reducing agent (atomic hydrogen), a complex additive  $TiO_2$ , a high molecular weight polymeric material can be applied in the course of modification, and microalloying [1].

Melting was conducted in a high-frequency induction furnace in an acidic lining. At the stage of metal finishing the alloying and modifying additives were introduced into the cast iron melt as bales (table 1).

The amount of the introduced additive  $TiO_2$  in different melts changed within the range 2.72 – 8.18%. The ratio of titanium oxide and high molecular compounds  $m_{oxide}/m_{hmc}$  was maintained constant in the bales, and it amounted to 3.75. The absorption of titanium from the oxide in the cast iron melt varies from 2.2% to 7.9%, while the increase of the additive  $TiO_2$  above 5.45 %wt. does not contribute to increase of the titanium concentration in the melt (table 2).

Relatively low rates of reduction are not primarily associated with low reducing capacity of the atomic hydrogen formed during the pyrolysis of rubber in the

melt; it can be explained by the increased melting loss of the reduced titanium. This is due to the relative longitude of melting blocks (about 10 min) containing titanium oxides and high molecular weight compounds (HMWC), at the stage of metal finishing.

The structure of the cast iron modified by titanium oxide was studied in accordance with the national state standard GOST 3443-87 (fig. 1-3, table 3).

The original alloy composition with 0.034% Ti (table 2) has the structure (table 3) with ferrite-pearlite base and lamellar graphite (fig. 1). Pearlite seems to surround the graphite plates. The rest is ferrite; cementite is formed in the center. There are also small inclusions of carbides in the structure.

The composition (table 4) and morphology of the formed non-metallic inclusions was determined with electron - probe EDX analysis on the IED detector 2201 when investigating the original and modified cast iron samples under SEM microscope JSM-5610LV (firm IEOL, Japan).

Detected with a microscopic analysis the carbide inclusions (fig. 1a, b) can be referred to (according to the results of scanning electron microscopy (SEM) to iron carbides (table 4) with dissolved copper (pos.1, fig. 1e). The obtained alloys (table 2) with the Ti content 0.070% (introduced 2.72 %  $TiO_2$ ), and 0.293% Ti (introduced 5.45%  $TiO_2$ ) resulted from the direct oxides reduction. In the alloy with 0,070% Ti (table 2), the alloy structure (fig. 2a, b) which is similar to the original one can be detected with metallographic studies (table 3). It is possible to differentiate (table 4) carbides (2 fig. 2c) and carbonitrides of titanium (pos.1, fig.2c) containing tungsten and vanadium (pos. 1 and 2, fig. 2b) with electron microscopic studies. Sulfur is in the form of sulfides of manganese (pos.4, fig. 2c). In pearlitic metal base of the cast iron there are compact carbides (size 0.3  $\mu m$ ) of cementite type (pos.1, fig. 2e) containing 1.59 % W and 0.19% V .

With increasing reduced titanium content to 0.290% and 0.293% (table 3) cast iron structure has the same form, but the amount of pearlite increases to P70 (fig. 3), but the dispersion of its components is significantly reduced. The structure of the metal base (fig. 3e) is differentiated only at high magnification ( $\times 5000$ ). This is ferrite-pearlite cast iron with the increased number of special carbides (TiC). Tungsten and vanadium are displaced from titanium by carbides (pos. 2 and 3, fig. 3e). There are separate compact inclusions of iron sulfides (pos.1, fig. 3e) and elongated sulfides of manganese (pos. 1, fig. 3c).

Introduction of the titanium from oxide provides increase of hardness (table 2) of cast iron HB from 1970 MPa (the modification was not carried out) to HB 2550 MPa (introduced 0.293% Ti) and even to HB 2850 MPa (introduced 0.290% Ti). The strength characteristics of the cast iron simultaneously increase from  $\sigma_t 149.0$  MPa (cast iron is not modified) to  $\sigma_t 196.0$  MPa (introduced 0.290% Ti). This is due to the increase in the number of pearlite constituent in the metal base of cast iron, the increase in the dispersion of the perlite, and the formation of a significant amount of fine titanium carbides.

TABLE I. TECHNOLOGICAL CHARACTERISTICS OF TITANIUM REDUCTION FROM OXIDES DURING CAST IRON DIRECT DOPING

Mass fraction of the introduced additive TiO <sub>2</sub> , % wt.	Block composition (TiO <sub>2</sub> + high molecular weight compound (HMWC))	Ratio m <sub>oxide</sub> /m <sub>HMWC</sub>	Introduced metallic Ti (from TiO <sub>2</sub> ), g	Introduced Hydrogen from HMWC, g	Introduced Carbon from HMWC, g	Metal recovery from oxide (in the cast iron composition), g	Metal recovery, %	The amount of metal which can be reduced by Hydrogen, g
2,72	600 g TiO <sub>2</sub> ; 160 g HMWC	3,75	360	28,32	C (atomic)-57,12 C (black)-60,32	7,92	2,2	679,68
5,45	1200 g TiO <sub>2</sub> ; 320 g HMWC	3,75	720	56,64	C (atomic)-114,24 C (black)-120,62	56,98	7,9	1359,36
8,18	1800 g TiO <sub>2</sub> ; 480 g HMWC	3,75	1080	84,96	C (atomic)-171,36 C (black)-180,94	56,32	5,2	2039,04

TABLE II. CHEMICAL COMPOSITION AND MECHANICAL CHARACTERISTICS OF THE CAST IRON MODIFIED BY TITANIUM FROM OXIDES

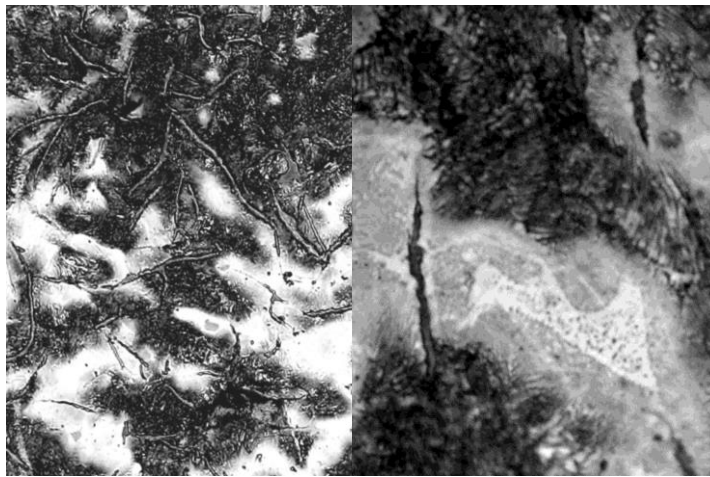
Mass fraction of the introduced additive TiO <sub>2</sub> , % wt.	Component Composition, % wt													
	C	Si	Mn	P	S	Mg	Cr	Ni	Mo	Cu	Al	Ti	V	Nb
Without additive	3,20	2,50	0,464	0,292	0,103	<0,001	0,075	0,043	<0,001	0,085	<0,001	0,034	0,015	0,001
2,72	3,19	2,35	0,430	0,278	0,102	<0,001	0,077	0,047	<0,001	0,085	<0,001	0,070	0,015	<0,001
5,45	3,20	1,97	0,369	0,306	0,123	<0,001	0,090	0,050	<0,001	0,087	<0,001	0,293	0,017	<0,001
8,18	3,20	1,72	0,299	0,321	0,125	<0,001	0,097	0,050	<0,001	0,089	<0,001	0,290	0,019	<0,001

CONTINUATION OF TABLE 2

Mass fraction of the introduced additive TiO <sub>2</sub> , % wt.	Component Composition, % wt											Mechanical Characteristics	
	W	Co	Zr	B	Ca	Sb	As	Sn	Pb	Zn	HB, MPa	σ <sub>B</sub> , MPa	
Without additive	0,017	0,002	<0,001		<0,0001	0,095	0,007	0,002	<0,001	≈0,052	1970	149	
2,72	0,019	0,003	<0,001		<0,0001	0,096	0,008	0,001	<0,001	0,048	2290	152	
5,45	0,030	0,003	<0,001		<0,0001	0,113	0,009	0,005	<0,001	0,027	2550	178	
8,18	0,032	0,003	<0,001	0,0102	<0,0001	0,110	0,008	0,005	<0,001	0,008	2850	196	

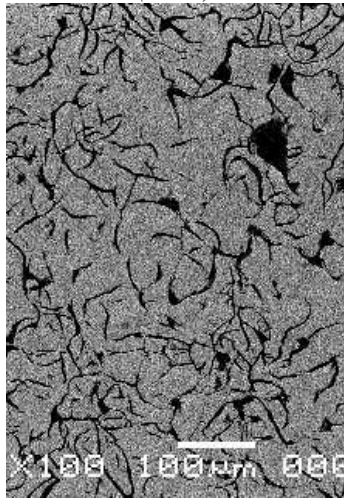
TABLE III. INVESTIGATIONS RESULTS OF THE CAST IRON STRUCTURE WITH TITANIUM OXIDE BALES AND HIGH MOLECULAR WEIGHT COMPOUNDS.

Mass fraction of the introduced additive TiO <sub>2</sub> , % wt.	Shape of graphite inclusions	Length of graphite inclusions	Distribution of graphite inclusions	Amount of graphite inclusions	Structure type of metallic base	Pearlite disperse-veness (PD)	Pearlite (P) and Ferrite (F) amount	Cementite (C) amount
Without additive	Plate direct PGph1	PGd90	PGr1	PG6	Pt1F	PD1.4	P45 (F55)	C10
2,72	Plate direct PGph1	PGd90	PGr1	PG6	Pt1F	PD1.4	P45 (F55)	C10
5,45	Plate direct PGph1	PGd90	PGr1	PG6	Pt1F	PD1.4	P45 (F55)	C10
8,18	Plate direct PGph1	PGd180	PGr1	PG10	Pt1F	PD1.4PD 0,3	P70 (F30)	C4

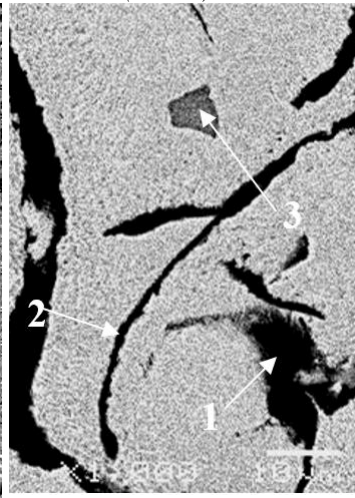


a ( $\times 250$ )

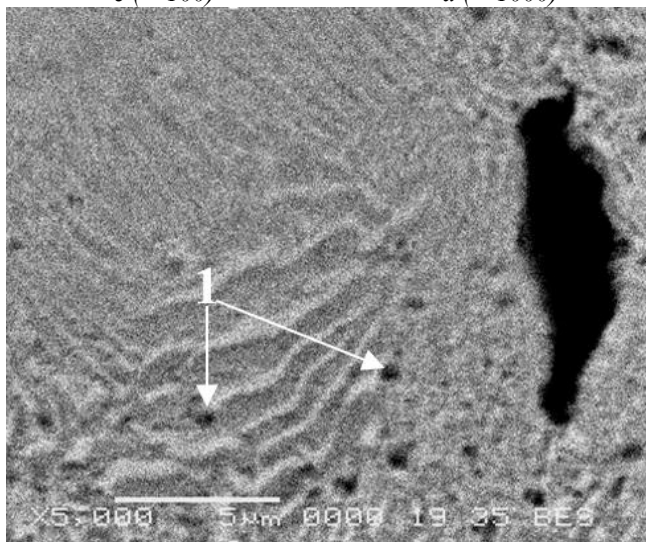
b ( $\times 1000$ )



c ( $\times 100$ )

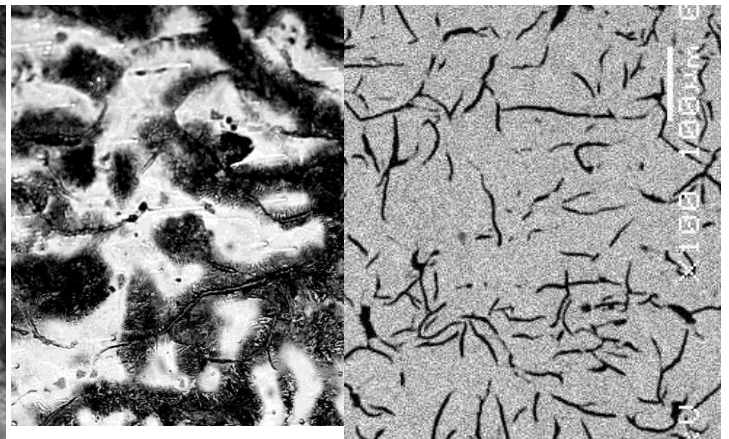


d ( $\times 1000$ )



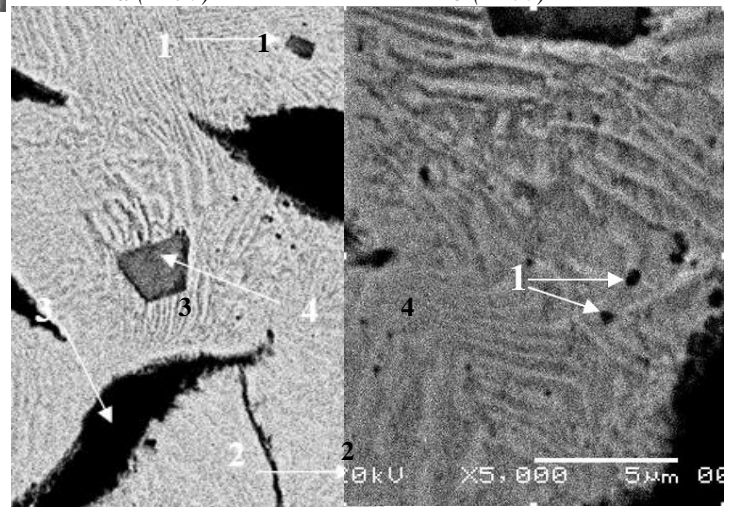
e ( $\times 5000$ )

**Fig. 1.** Microstructure of the original cast iron (etched specimen): a,b – metallographic investigations; c, d, e – investigations by scanning electron microscopy.



a ( $\times 250$ )

b ( $\times 100$ )



c ( $\times 2000$ )

e ( $\times 5000$ )

**Fig. 2.** Microstructure of the cast iron with 0.070% Ti (introduced 2.72%  $\text{TiO}_2$  (etched specimen)): a – metallographic investigations; b, c, e – investigations by scanning electron microscopy.

### III. CONCLUSION

The basic principles of creating complex resource-saving metallurgical technologies for the production of high-quality alloys for modification and microalloying by chemical interaction of the introduced additives with certain elements of the crystallizing substance using industrial waste and intermediate products related to mechanical engineering industries are considered in the paper. The new scientific information about the peculiarities of structure and properties of alloys, including the nature of the distribution between the phases of both core and other elements-admixtures, accidentally or deliberately introduced into the melt in the process of deoxidation, modification, or microalloying, microcomposition, and nature of non-metallic inclusions.

The titanium introduction in the melt by the method of direct doping saves expensive and scarce ferroalloys.

Unlike the known modification methods of cast iron from ferrotitanium, when the modifying effect is explained by the deoxidizing titanium action, in the course of direct doping, in the presence of such a strong reducing agent as atomic carbon, the crucial modifying effect is provided by carbide inclusions.

TABLE IV. CHEMICAL COMPOSITION AND MECHANICAL CHARACTERISTICS OF THE CAST IRON MODIFIED BY TITANIUM FROM OXIDES

Mass fraction of the introduced additive TiO <sub>2</sub> , % wt	Position of the inclusion	Component composition, % wt.											
		C	O	Si	Mn	S	Cr	W	V	Ti	Cu	N	Fe
Without additive	1 (fig. 1d)	74,36	-	0,42	1,25	0,06							23,92
	2 (fig. 1d)	25,20		1,82	4,20	0,55			0,12				68,02
	3 (fig. 1d)				64,87	35,13							
	1 (fig. 1e)	6,34		1,83	4,47	0,15			0,27		3,03		83,92
2,72	1 (fig.2c)	7,34						1,09	1,40	35,81		2,14	52,22
	2 (fig. 2c)	10,15						2,06	3,97	35,08			48,75
	3 (fig. 2c)	85,01							0,15				14,83
	4 (fig. 2c)				65,19	34,49				0,32			
	1 (fig. 2e)	4,26						1,59	0,19				93,96
5,45	1 (fig. 3c)	15,73	0,85		46,83	27,59	2,73	0,23					6,04
	1 (fig. 3e)	1,70		1,62		8,03				22,63	0,12		65,90
	2 (fig. 3e)	19,45		1,04		7,19				20,13			52,19
	3 (fig. 3e)	16,85		1,14		2,31				6,28	2,87		70,55
	4 (fig. 3e)	92,01			0,73	0,18	0,29		0,09				6,69

References:

[1]. Harast A. I. Zhelezouglerodistyeplyavy: strukturoobrazovanie i svoystva [Iron-carbon alloys: structure and properties]. / A. I. Harast. – Minsk: Belarus. navuka, 2010. – 252 p. (in Russian).

[2]. Harast Aliaxandr Ivanovich. 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.

[3]. Sposoby plavki chuguna i sposoby plavki stali. [Method of iron smelting and steel production]: pat. 11641 Resp. Belarus: MPK (2006) C 21 C 1/00, C 21 C 5/00, F 23 G 5027 / A. I. Harast; appl. EI «Bel.gos. tehnol. un-t». – № a20050280; appl. 24.03.2005; publ. 30.12.2006 // Aficyjny bjuletjen' / Nac. Cjentr intjelekt. ulasnasci. [Official Bulletin. Centre of Intel. Property]. – 2009. – № 1.

[4]. Lekah, S. N. Legirovanie chuguna iz shlakovoj fazy [Alloying of cast iron from slag phase]. / S. N. Lekah, A. G. Sluckij, V. L. Tribushevskij // Litejnoe proizvodstvo. [Foundry]. – 1985. – vol. 10 – p. 10.

[5]. Bobro, Ju.G. Zharostojkie i rostostojkivye chuguny. [Heat-resistant

and stable cast irons]. / Ju. G. Bobro. –M. –Kiev: Mashgiz, 1960. – 170 p.

[6]. Gol'dshtejn Ja.E, Mizin V.G. Modificirovanie i mikrolegirovanie chuguna. Modification and microalloying of iron. [Modification and microalloying of cast iron]. – M.: Metallurgija. 1986. – 272 p. (in Russian)

[7]. Harast A.I. Mehanizm strukturoobrazovanija v jekonomno legirovannyh iznosostojkivych chugunah. [The mechanism of structure formation in alloyed wear resistant cast iron]. Lit'eim metallurgija [Casting and metallurgy], 2012, vol. 3. – p. 101-113.

[8]. Harast A.I., Goreckij G.P., Vajsova V. V., Pavlovich V.G. Uluchshenie struktury i svoystv Fe-C splavov pri prijamom legirovanii. Metallurgijamashinostroenija. [Improvement of structure and properties of Fe-C alloys by direct alloying. Metallurgy engineering]. – 2011, vol.3. – p. 15-18.

[9]. Aliaxandr I. Harast. Modification and Microalloying of Iron Carbon Alloys Using Industrial Polymer Scrapes. Journal of Current Advances in Materials Sciences Research. (CAMSR). Volume 1, Issue 3 Dec. 2014 PP. 66-74 www.vkingpub.com/journal/camsr/© American V-King Scientific Publishing.