

Morphological forms of carbon and their utilizations at formation of iron casting surfaces

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Abstract

Model pyrolysis made possible to identify three solid products of carbonaceous additives. Lustrous carbon is the most important form of the pyrolysis carbon. With its structure and physical and chemical properties it comes near to graphite. Amorphous carbon with turbostratic lattice, higher oxireactivity, and lower protective function against liquid metal comes near to carbon black. Semicoke also plays a non-negligible role. All forms of carbon have an important representation in oolitized quartz grain also during forming the casting surface. While amorphous carbon is formed directly from the gaseous phase by homogeneous nucleation, lustrous carbon, with regard to similarity of lattices with quartz, is formed by heterogeneous nucleation on grains. High covering power and low oxireactivity give its highest protecting power of the mould face. New experimental equipment made possible to check a possibility of use of new composite bentonite binders containing „process carbon“ (graphite, anthracite, amorphous carbon). The BTEX content in exhalations and in waste sands too was considerably decreased with high smoothness of castings.

Keywords: Product development; Environment protection; Lustrous carbon; Amorphous carbon; Semicoke; Heterogeneous/homogeneous nucleation; Mixed Bentonite; Casting smoothness; BTEX.

1. Introduction

Positive effect of black coal on surface quality of castings from graphitizing ferrous alloys is known since 18th century. It is gradually explained by a number of theories from counter pressure of gases, the formation of a gas cushion, clogging of mould pores, reducing atmosphere, up to „the lustrous carbon theory“ [1]. I. Bindernagel [2] has extended the theory on the so called „theory of complex effect of carbonaceous additives“ containing not only the lustrous carbon (exactly the pyrolysis carbon – PC) but thermoplastic properties of coke and the action of gas components too.

The main effect of coal and carbonaceous additives (C-additives) is put in connection with metallobitization of the green mould face caused by the presence of copyrolysis products. Efficiency of lustrous carbon (LC) carriers grows with the amount of liberated PC. Coal is therefore enriched with further organic matters (natural and synthetic resins) with the aim of increasing the LC share at reduction of the content of bentonite mixtures additives. On the contrary it brings the increase particularly of aromatic hydrocarbons in gaseous exhalations and waste sands and the deterioration of hygienic and ecological impacts in foundries.

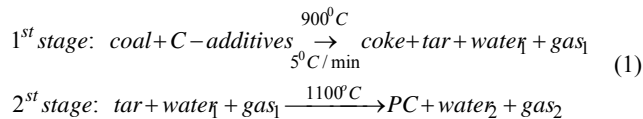
Present research [3-7] is aimed at reduction of pollutants concentration in working environment of foundries liberating

from foundry moulds particularly when pouring and knocking out of castings by replacement particularly of coal and C-additives with high content of aromates with keeping high quality of iron casting surfaces.

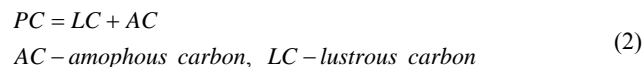
Our research is aimed at identification of morphological forms of carbon forming during pyrolysis processes of C-additives, determination of their roles in forming casting surfaces and possibilities of their direct utilization for preparation of composite bentonite binders of a new generation with simultaneous decrease of hygienic and environmental burdens of foundry manufacture (criteria BTEX in particular).

2. Pyrolysis of carbonaceous additives

Two-stage pyrolysis was studied on a laboratory model unit [8]. A black coal sample and C-additives, e.g. natural resin-colophony (K), gilsonite (G), indene-cumarone resin (IK)-tar derivate were used for copyrolysis:



Pyrolysis carbon (PC) has two quite morphologically different forms:



what enables their semiquantitative separation too. The yield of LC and of AC too grows in the sequence as follows: coal < IK < K < G. Semicoke represents the third solid form of carbon from pyrolysis reaction of C-matters. Gas₁ is a mixture of aromatic and aliphatic hydrocarbons; gas₂ represents simple gases difficult to decompose (CO₂, CO, H₂, CH₄...).

3. Morphological forms of pyrolysis carbons

All the three forms of quite different physical and chemical properties (see Tab. 1.) play their irreplaceable role in forming of casting surfaces:

Table 1.
Physical and chemical properties of pyrolysis products

	Semicoke	AC	LC
Density [g.cm ⁻³]	1.81	1.92	2.10
Aromaticity [H ^{at} /C ^{at}]	0.155	0.072	0.037
Oxireactivity [°C]	574	630	807

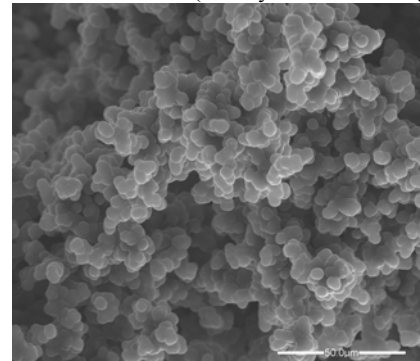
Amorphous carbon (AC) (see Fig. 1a.) represents well degasified carbon (V^{daf} = 0.8 – 1.6 %, ISO 562:1981) containing 97 – 98 % C and 0.5 – 0.7 % H₂.

Its typical spheroidal morphology forms grapy formations. Real density had a value of 1.89 – 1.95 g.cm⁻³, mean aromaticity of 0.072 and oxireactivity (measured thermogravimetrically) about 630 °C (according to TGA).

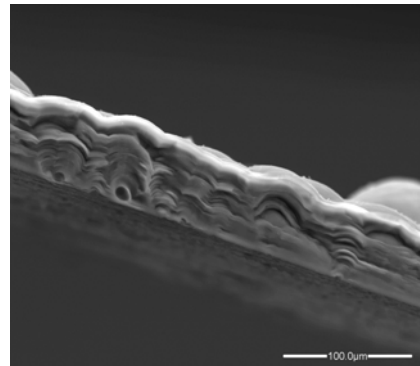
Amorphous carbon is a majority component of pyrolysis carbon (PC). It is formed by homogeneous nucleation directly from the gaseous phase. With its physical and chemical character it comes near to carbon black.

Lustrous carbon (LC) (see Fig. 1b.) forms a highly compact film with immeasurable volume of pores, highly degasified minority part of PC (0.23 – 0.37 % H₂) with mean aromaticity of 0.037 and lowest oxireactivity about 807 °C. It has the highest arrangement of carbon substance (density of 2.08 – 2.13 g.cm⁻³).

a)



b)



c)

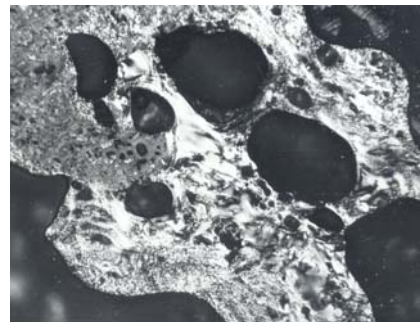


Fig. 1. Pyrolysis forms of C-additives (1a - AC, 1b - LC, 1c - semicoke),

With regard to similarity of LC and quartz lattices it is formed by heterogeneous nucleation with high adhesion to quartz base sand. With its hexagonal lattice it comes near to graphite.

Coke (semicoke) (see Fig. 1c.) represents the highest share from pyrolysis processes of C-additives of bentonite mixtures. It has the highest oxireactivity (574 °C), the lowest aromaticity (0.155) and the lowest density (1.81 g.cm⁻³).

During thermal exposure of the mould with C-additives the oxidation character of green bentonite mixture is changed to the reduction one with simultaneous oolittization of quartz grains by pyrolysis products. In the zone of highest temperatures a highly stable film is formed that is non-wetting by metal and has high adhesion to quartz base sand (see Fig. 2.).

AC and the coke with higher oxireactivity are partly burned and they protect moulds in greater depths only. The effect of coke consists in choking the pores and compensation of stress from thermal expansion of quartz base sand (plastic state of coal, swelling index).

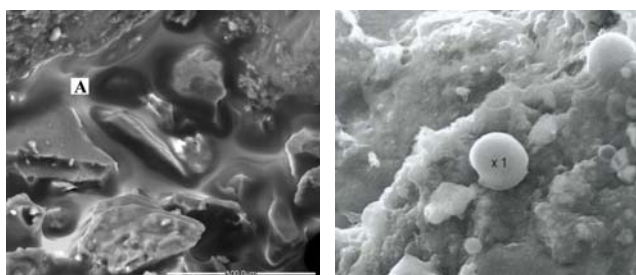


Fig. 2. Film LC a zbytky AC (kuličky) na líci reálné bentonitové formy po odlití

4. Function of graphite in bentonite mixture

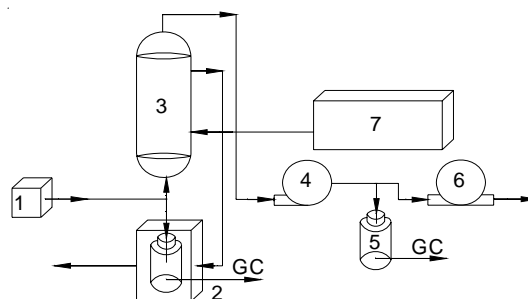
In 1987 the additive of natural or synthetic electric graphite to bentonite binders was patented that would accelerate water adsorption by montmorillonite. It is based on a presumption of similar stratified structure and an idea of putting the montmorillonite basal planes off. The main declared effect consists in higher strength of the mixture in the water condensation zone [9].

According to the customer's wishes the firma Süd-Chemie (GER) prepares bentonite with a graphite additive (Geko optimum) which plays here a function of „a gliding agent“ (Gleitmittel). In this respect the longest way has gone the firm S – B Industrial Minerals (IKO – Marl, GER) that uses microcrystalline graphite in a developmental series of bentonite binders as follows: ANTRAPUR, POLYCARBON, PRIOCARBON, a new composite bentonite binder ENVIBOND containing besides high quality bentonite also graphite, inorganic buffers and additives compensating stress from thermal expansion of quartz with considerably decreased BTEX content [10].

A question comes on offer how much can be achieved the mould metallofobization (oolittization of grains) with the aid of composite bentonite binder containing so called „process carbon“ (graphite, anthracite, AC) with considerably decreased volume of pollutants and keeping the casting smoothness (partial or total replacement of coal with C-additives).

5. Experimental equipment

Experimental equipment can be divided in two parts , a mould with a test casting and a mobile cover, an apparatus for taking of liquid and gaseous (steam-gaseous) components (VOC) (Fig. 3.). A model equipment makes possible to change thickness of the test iron casting (EN GLJ-200, constant temperatures 1342 – 1369 °C in a ladle) and in such a way the thermal stress of the mould too (mould/metal = 2 ÷ 22). Casting smoothness is evaluated with the aid of a SVÚM standard by a comparative method and surface measurement from the core (Mitutoyo Surfrest – 211) that is compacted from the mixture of the same composition as the mould but to a constant defined compacting degree. The mould is covered with the mobile cover making possible to catch and exhaust the pollutants after casting the mould and during knocking out the casting.



- 1 - VOC source
- 2 - cool sample
- 3 - cooler
- 4 - air pump
- 5 - control sample
- 6 - wet gas - meter
- 7 - cooling agent source

Fig. 3. Taking of equipment

Pyrolysis gas liberated by the mould is sucked in a cooler and in the obtained condensate the concentration of organic pollutants, in particular of BTEX, is determined with the aid of gas chromatography (GC). For checking the total condensation of organic vapours there is incorporated, behind the pump, the second check sample that is also analysed with the aid of GC. The core also facilitates the thermal field gauging, the movement of the water condensation zone, the degree of C-additives degradation and of montmorillonite dehydroxylation, and determination of BTEX in waste mixture.

6. Results of experiments

Influence of partial replacement of C-additive (18 % PC) by graphite and anthracite additives on BTX and TOC was studied in particular. Given composition of bentonite mixture and their concentration were chosen in such a way that the smoothness of casting surface was comparable in all cases (Tab. 2).

Table 2.
Concentration of pollutants at partial replacement of the C-additive by graphite and anthracite

Composition of mixture	Mixture moisture [%]		VOC [mg] ⁺⁾	
100 w. p. SiO ₂ 8 w. p. Na-bentonite C-additive = 0.4 % PC	4.0		B	705.27
			T	185.94
			X	28.32
			TOC	1315.8
100 w. p. SiO ₂ 8 w. p. Na-bentonite C-additive = 0.2 % PC 0.3 w. p. graphite	4.0		B	25.5
			T	4.2
			X	1.2
			TOC	95.7
100 w. p. SiO ₂ 8 w. p. Na-bentonite C-additive = 0.2 % PC 0.1 w. p. anthracite	4.0		B	59.4
			T	11.7
			X	3.3
			TOC	257.1

+) determined in volume of sucked gas (40l)

The addition of both graphite and anthracite too with reduction of C-additive to a half means considerable reduction of pollutants (BTX) content and of total organic carbon (TOC) too.

In the second case new composite bentonite binders marked A and B (Tab. 3) were prepared. In case of A binder a special treatment technology of bentonite – graphite paste was used that was after drying ground to the same fineness of the original Na – bentonite (Na – bentonite $d_{50} = 34.2 \mu\text{m}$, bentonite + graphite $d_{50} = 39.2 \mu\text{m}$). In case of B binder a special amorphous carbon (AC) was used in the weight ratio to bentonite 1: 8. Thermal stress of the mould corresponded to the $f/k = 2.05$ ratio. In addition to it a regard was paid to the fact that all mixtures had the same moisture and compaction degree, i.e. 3.5% or 1.6 g.cm⁻³ respectively. With new binders the extremely smooth casting surfaces were obtained. Especially important was the BTX reduction in waste mixtures what is the way to the environmental friendly technologies with use of new composite bentonite binders.

Table 3.
Influence of new bentonite composites on smoothness of castings and VOC in waste sands

Composition	Smoothness Ra		BTEX [mg/kg]	
	[μm]			
	1)	2)		
100 w. p. SiO ₂ 7 w. p. Na-bent.	16-25	25.34	B	7.62
			T	22.31
			E	2.17
			X	21.56
100 w. p. SiO ₂ 8.5 w. p. A	10-16	15.69	B	1.26
			T	5.14
			E	0,56
			X	8,07
100 w. p. SiO ₂ 8 w. p. B	6.3-10	16.48	B	0.06
			T	0.15
			E	0.09
			X	0.33

1) SVUM standards

2) Mitutoyo Surfrest-211 ($\phi 5$ measured points)

7. Conclusion

Modelling of the two-stage pyrolysis made possible to identify three solid morphological forms of carbon influencing the surface formation of castings from graphitizing ferrous alloys. They are a part of oolitized quartz grains in green bentonite mixtures. Pyrolysis of C matters also brings the formation of pollutants with negative impacts on hygiene and ecology of foundry manufacture.

New experimental equipment enables the development and testing of new composite bentonite binders and their influence on reduction of BTX content in emissions and waste sands with keeping high quality of casting surface. In this respect the first composition variants resulting from the so called „process carbon“ (graphite, anthracite, amorphous carbon) were successfully checked.

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