Brief note

ON INCREASING POWDER CARBON STEELS PROPERTIES USING ACTIVATING ADDITIVES

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In this paper, the possibility of increasing powder carbon steels properties by activation of carbon diffusion into the iron base during sintering process due to the introduction of the thermally split graphite (TSG), macromolecular compounds (MC) and sodium bicarbonate was investigated. It was found that the introduction of these additives allows obtaining homogeneous structures at a sintering temperature of 100–200 °C lower than that traditionally used for sintering of powder carbon steels. Such structures provide increased mechanical properties of powder carbon steels. The addition of sodium bicarbonate increases the diffusion rate of carbon into iron at a temperature of *950 C* by 1.8 times, at *1000 °C* by 1.5 times, and at 1100 °C by 1.2 times.

Key words: powder carbon steels, activating additives, structure, mechanical properties.

1. Introduction

Powder metallurgy is one of the most progressive processes for parts manufactured for various purposes. Numerous technological processes of powder metallurgy can reduce the consumption of materials, manufacturing energy and allow automation of the process. The necessary combination of manufacturability and reliability of parts, as well as obtaining the required material properties, are ensured by controlling the processes of structure formation.

The structure and properties of powder carbon steels, in which carbon is the main alloying element, depend on the degree of homogeneity of the structure formed during sintering. It is due to diffusion processes, which are determined by the structure, dispersion and the degree of oxidation of iron particles and carbon additives, the components relative volumes, sintering conditions and the atmosphere composition. By changing these factors, it is possible to get a diverse combination of structural components.

Carbon is introduced into powder materials by mixing the initial powders. Graphite with various structures, carbon black and nanocarbon powders are used as carbon additives. According to Jonnalagadda [1] and Hryha *et al.* [2], the most common carbon additives are powders of various modifications of natural graphite as well as synthetic graphite. They differ in their purity level, crystallographic structure (size and orientation of crystallites), and particle morphology. The activity of carbon-containing additives has an important role in the structure formation of powder carbon steels. This activity has a significant effect on the reduction of oxides that are present on the surfaces of iron and alloying elements particles. According to Zhang *et al.* [3] as well as Hryha *et al.* [4], synthetic graphite has high reactivity at sintering process and provides higher mechanical properties of powder steel.

The dissolution of graphite in an iron matrix, as was shown by Danninger *et al.* [5], occurs initially during the transition of carbon atoms through the contact areas formed in the pressed part, and then during the transition through the contact areas formed during sintering. During iron carbonation with graphite, a solid solution of the carbon in γ-iron and cementite were formed at temperatures above the α→γ phase

transformation. Moreover, according to Gilardy *et al.* [6], the diffusion process cannot be realized completely and is not capable of restoring and saving contacts between surfaces of graphite and iron particles during sintering. It is the result of a decrease in the volumes of dissolved graphite particles. Therefore, by regulating the contact between iron-carbon surfaces, it is possible to control the process of structure formation in the powder steel.

According to Gilardy *et al.* [7], the rate and degree of the graphite dissolution increase with decreasing graphite particles size and increasing its activity during formation of atomic carbon. Atomic carbon is formed as a result of oxidation-reduction reactions. Tanaka *et al.* [8] reported that oxides, which are present on the iron particle surface, are reduced by reacting with the carbon contained in the iron powder and graphite. Oxygen is removed in the form of CO_2 which decomposes with the formation of atomic carbon, according to the Boudoir reaction.

In the case of iron powder pre-alloyed with chromium, the surface oxides consist mainly of a layer of iron oxides with some more stable finely divided chromium oxides. For the effective reduction of such oxides, Hryha *et al.* [9] used graphite and atmospheres of various compositions. The results showed that the combination of a dry hydrogen-containing atmosphere and fine graphite particles allows the reduction of chrome oxides and ensures successful sintering of powder chromium steels.

In the work of Dorofeev *et al.* [10] the influence of the graphitization degree of a carbon based additive on the sintering process of powder carbon steel was investigated. It was shown that low-ash graphite, pyrocarbon, and high-temperature coal tar pitch are the most promising. When using synthetic graphite and high-temperature coal tar pitch, the surface diffusion is the main sintering process. The volume diffusion and viscous flow are the main factors affecting the sintering process of pyrocarbon and natural graphite

To improve the properties of carbon powder steels, Eremeeva *et al.* [11] introduced carbon in the form of nanopowders. However, it was impossible in this case to obtain a homogeneous structure during sintering due to the irregular distribution of carbon in the powder mixture despite the high activity of nanopowders.

Gilardi *et al.* [12] used the mechanical activation of tungsten carbide powder and a mixture of tungsten oxide and various carbon grades to accelerate recovery processes.

Thus, the activation of diffusion processes during the sintering of powder carbon steels is possible due to the introduction of carbon in the form of an active carbon-containing additives or the introduction of additives that cause oxidation-reduction reactions, resulting in the formation of atomic carbon, which actively diffuses into the iron base.

The aim of this work is to study methods for activating the carbon diffusion process into an iron base during sintering of powder steels by introducing of thermally split graphite (TSG), macromolecular compounds (MC) and sodium bicarbonate.

2. Experimental procedure

The sprayed iron powder with an average particle size of *160* μ*m* was used as the base of powder steels. Graphite, thermal split graphite (TSG), macromolecular compounds (MC) were used as a carbon-containing additive, and sodium bicarbonate was used to activate oxidation-reduction reaction and diffusion processes.

The iron powders and 1 wt. % carbon were mixed in a mixer of "drunken barrel" type for *3 h*. Then, the samples were pressed in a hydraulic press to achieve a relative density of *80–83%* and sintered in an endothermic gas consisting of *20 %* CO, *40 %* H_2 and *40 %* N_2 at *800–1150 °C* for *1 h*.

TSG was obtained using layered graphite compounds (LGC). This compound is the result of the inclusion of various substances (alkali metals, acids, metal chlorides, etc.) in the interlayer spaces of a graphite lattice. The introduction of these substances leads to a distortion of the graphite lattice, the breaking of weak bonds and the formation of layered compounds of the $C_xM_eCl_y$ type. The TSG structure varies depending on the number of planes of carbon atoms with a hexagonal bond per layer of substance. TSG was obtained by mixing graphite with iron chloride in a ratio of 1:1 as well as graphite with nickel or cobalt

chloride in a ratio of 1:3. The mixture was placed in a furnace and kept in a flow of chlorine for *15–20 h* under a temperature of *250–300 °C* when using iron chloride and under *550–600 °C* when using cobalt or nickel chlorides. TSG was obtained by pyrolysis of LGC under temperatures of *800–900 °C* with $FeCl_3$ and under *900–1000 °C* with $NiCl_3$ or $CoCl_2$. TSG with embedded iron chloride of I, II, III stages, cobalt chloride of I and II stages, nickel chloride of the II stage were used.

Polydiethylene glycol adipates, polypropylene glycol adipates, polypropylene glycol succinate, polypropylene glycol sebacinate were used as MC. The basis of these compounds is ethylene glycol having the melting point of *12.7 °C* and the boiling point of *~ 197.6 °C*. Its formula is

$$\triangledown + CO_2 \longrightarrow \left[\begin{array}{c} O \\ O \end{array}\right] = O \xrightarrow{-CO_2} \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} \tag{2.1}$$

These compounds have a liquid state at room temperature, which simplifies the process of their introduction into the powder mixture.

To obtain a more uniform distribution of additives in the mixture, a ligature of *50%* iron and *50%* MC was preliminarily prepared. The content of the MC in the powder steel was *1%*.

The activating effect of sodium bicarbonate on the dissolution of graphite was determined using radioactive analysis. This method is based on determining the concentration of isotopes at different depths of the diffusion zone after removing each subsequent layer of the material. The specific radioactivity of the layer removed was determined by the difference in the integrated radiation intensity of the sample before and after layer removing.

For testing, samples of iron powder or iron with an additive of sodium bicarbonate were used. Samples were carburized in a solid carburetor with the addition of the C_{14} radioactive isotope in the form of $Ba_{14}CO_3$ or elemental C_{14}. The study of carbon diffusion was carried out by the method of integral residues. A layered radioactive analysis was carried out after removing layers of *5–10 µm* thickness in the direction perpendicular to the diffusion front by measuring the integrated radioactivity using a T25–BFL counter on a DP–100 radiometer. The measurement error was of *1.5%*.

The effective diffusion coefficients of carbon in iron powder were calculated using concentration curves under the temperature range of *950–1100 °C*.

The material structure was studied using an MEF–3 metallographic microscope. Cross-sections were etched with a *4%* solution of picric acid in ethyl alcohol.

The compressive strength studies were carried out with a universal testing machine "Tinius Olsen H150K–U" with a loading speed of *2 mm/min*. Hardness was determined using a Brinell tester with a ball of a *2.5 mm* diameter and a load of *187.5 N*.

3. Results

3.1. Study of the TSG introduction

The studies of the particle shape confirmed that the TSG powders are active due to the high unit surface area. In contrast to pencil graphite with a fragmentation form of particles, TSG particles have a layered structure (Fig.1).

The content and type of the compound introduced into the TSG affect the carbon content in the powder steel (Fig.2). The maximum carbon content is achieved by introducing TSG with stage II iron chloride and stage I cobalt chloride, since these powders have a larger unit surface area and contain less chlorine as oxidizing agent. When sintering, both atmospheric carbon and the carbon additive are used for the chloride reduction. This is especially evident at high temperatures, when reduction processes occur most actively.

The activity of TSG provides the formation of a pearlite structure at a lower sintering temperature. A microstructural analysis showed that when TSG is introduced, *40%* pearlite is present when sintering at *800°C*, while at *900°C* a homogeneous pearlite structure is formed and free graphite is absent (Fig.3). With the introduction of pencil graphite at a sintering temperature of *800°C*, the pearlite content is of *20%*, at

900°C is equal *40%* and the basis are ferrite and graphite. This is explained by the fact that under TSG decomposition at a temperature of *800°C*, the active carbon atoms diffuse into iron intensively.

At the same time, the introduction of TSG decreases the technological properties of the mixture: the fluidity decreases 2–2.5 times, and the bulk density is reduced 3–4 times compared to pencil graphite. Due to the complexity of the pressing process, it is impractical to use them as a carbon additive to powder steels for high-performance production.

Pencil graphite	TSG with $FeCl_3$ II stage
TSG with $CoCl_2$ I stage	TSG with $CoCl_2$ II stage
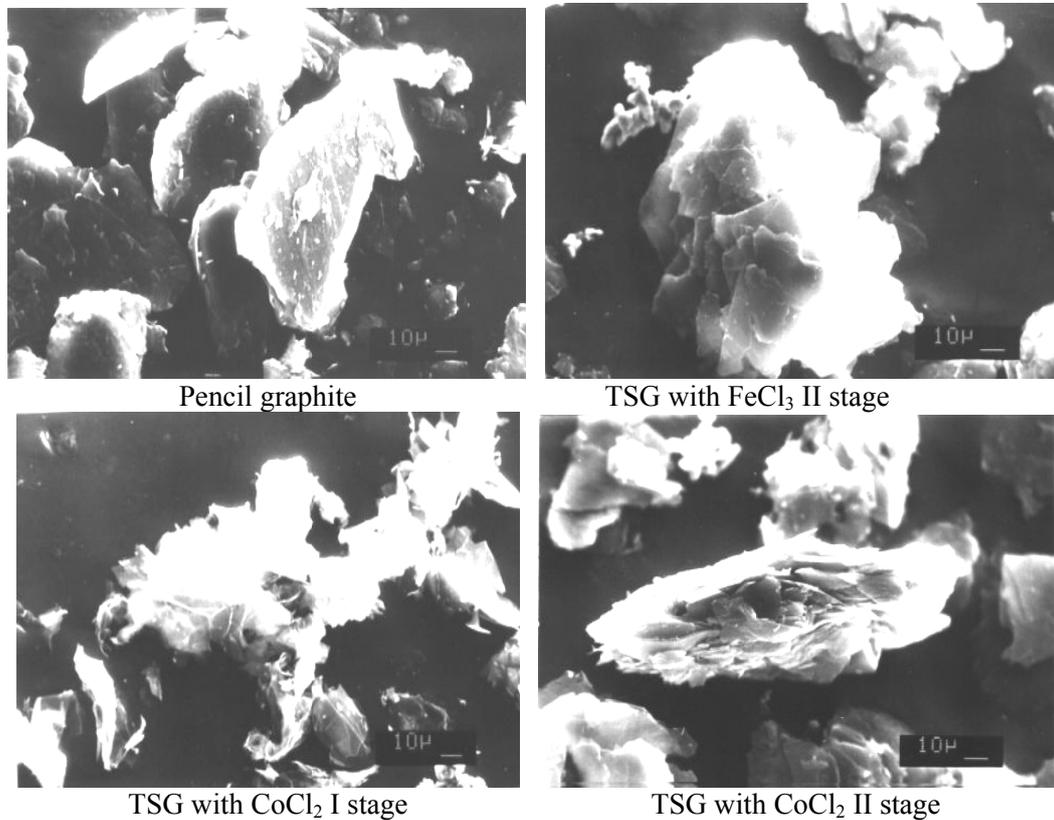
Fig.1. Particle shapes of pencil graphite and TSG powders.
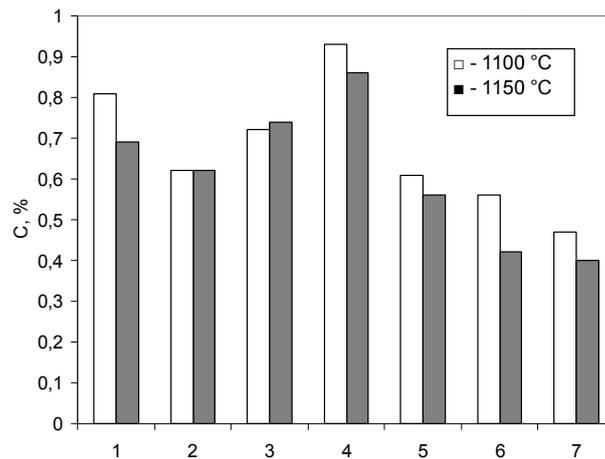
Fig.2. The influence of the TSG type and sintering temperature on the carbon content in powder steel:
1 – TSG with $FeCl_3$ stage I; 2 – TSG with $FeCl_3$ stage II; 3 – TSG with $FeCl_3$ III stage; 4 – TSG with $CoCl_2$ stage I; 5 – TSG with $CoCl_2$ stage II; 6 – TSG with $NiCl_3$ stage II; 7 – pencil graphite.

TSG with CoCl$_2$ I stage, *800°C*   TSG with CoCl$_2$ I stage, *900°C*

Pencil graphite, *800°C*   Pencil graphite, *900°C*
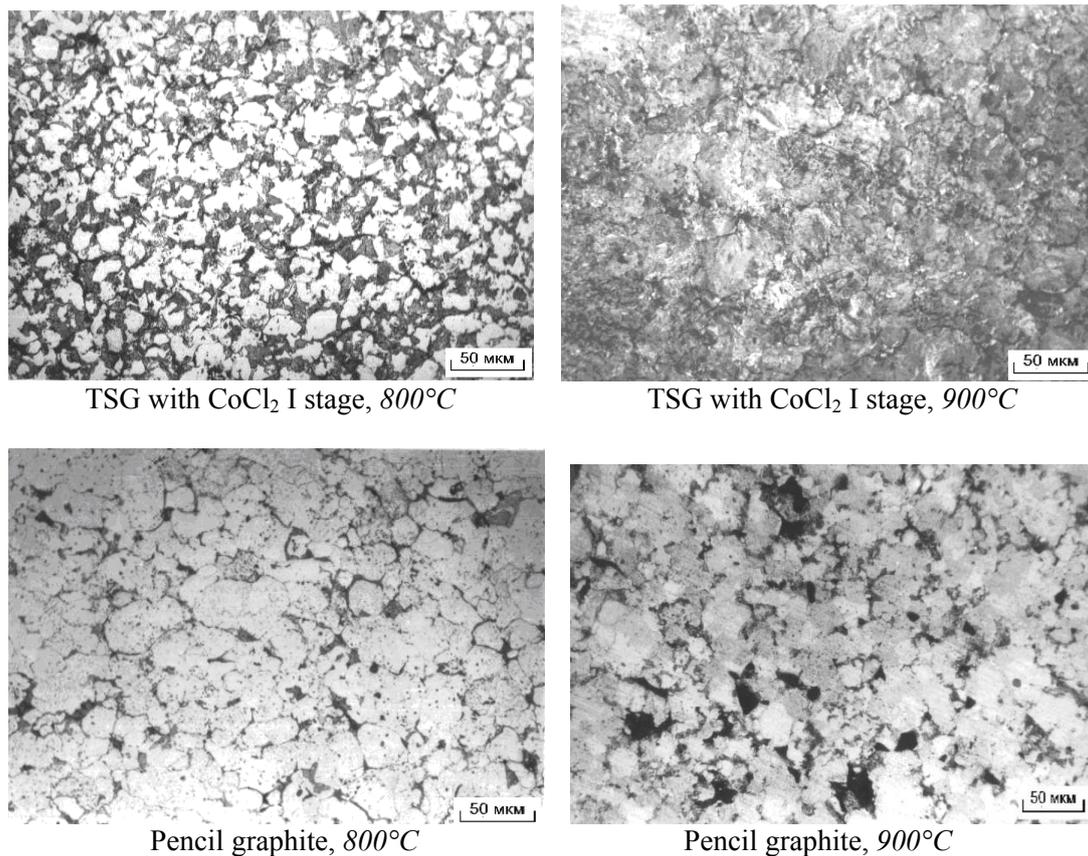
Fig.3. Structure of powder carbon steel sintered in endothermic gas.

3.2. Study of the MC introduction

The introduction of MC additives that decompose when heated is a very promising method for producing active atomic carbon. In addition, MC acts as lubricant during pressing.

A study of the compressibility of iron with MC additives showed (Fig.4) that the compounds introduced make it possible to obtain a higher density than the standard addition of zinc stearate with all pressures tested. The maximum density (*7 g/cm^3*) was achieved with the introduction of *1%* polydiethylene glycol adipate.

During sintering, due to the formation of a liquid phase during MC melting, powder steel samples are characterized by shrinkage, which is practically independent of the sintering temperature, since the liquid phase appears already at low temperatures (Tab.1).

Metallographic analysis showed that when adding MC there is pearlite in the iron structure sintered at *900°C* due to the diffusion of atomic carbon formed because of the additive decomposition (Fig.5). The amount of pearlite depends on the type of compound. The highest content of pearlite is observed with the introduction of polypropylene glycol adipate and polypropylene glycol succinate (Fig.5). The introduction of MC into the iron-graphite composition is especially effective, because the dissolution of graphite in iron is activated and free graphite is not observed under sintering at *900°C*. The highest carbon content was observed at the boundaries of the iron particles where the MC additive was located. Structural changes are not detected with increasing sintering temperature to *1100°C*.

An increase of sintering temperature does not affect the hardness of iron, and only a slight increase of compressive strength was noted (Fig.6). This suggests that even at a sintering temperature of *900°C*, full diffusion processes and complete volume changes take place. It should be noted that iron properties depend

on the MC type. The use of polyethylene glycolsebacinate leads to a slightly lower strength and hardness of iron.
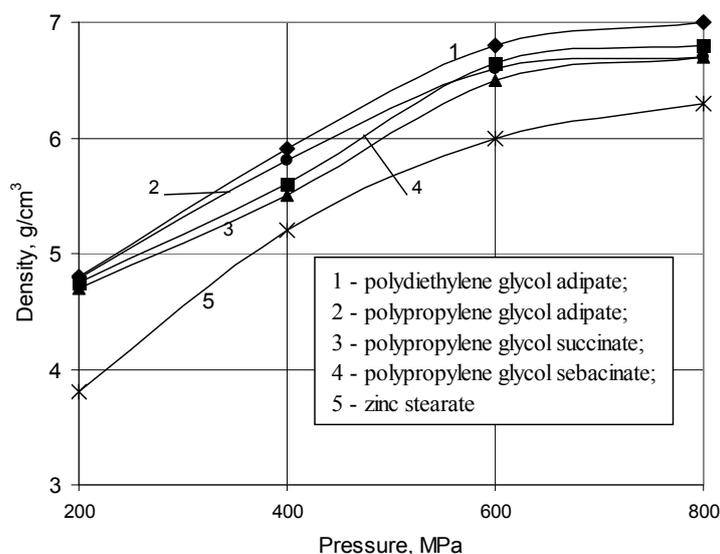
Fig.4. The dependence of the green density of powder steel samples on pressure values.

Table 1. Volumetric shrinkage changes after sintering of powder steel samples.

Macromolecular compound	Volumetric shrinkage, %	
	900 ℃	*1100 ℃*
Polydiethylene glycol adipate	*0.6*	*0.6*
Polypropylene glycol adipate	*0.2*	*0.3*
Polypropylene glycol succinate	*0.4*	*0.5*
Polypropylene glycol sebacinate	*0.7*	*0.8*
Zinc stearate	*0.1*	*0.1*

Thus, the addition of macromolecular compounds helps accelerate the diffusion of carbon due to the formation of atomic carbon caused by decomposition of these compounds. It also improves the compressibility of the iron powder.

3.3. Study of the introduction of alkali metal compounds

It was shown in Lanskaya *et al.* [13], as well as in Axelrod *et al.* [14] that microadditives of rare-earth and alkali metals are introduced into cast steels to modify the structure. Alkali metals are more active. However, they have lower densities in comparison with rare earth metals; therefore, they are not widely used in metallurgy. The introduction of alkali metal additives was also practically not used in powder metallurgy. It was indicated by Wang *et al.* [16] that alkali metal additives have high chemical activity and strong horophilicity to iron. The low melting temperature of some compounds of alkali metals allows activating the sintering process due to the formation of a liquid phase. In addition, they are good reducing agents.

According to Mukerji *et al.* [17], treating of low-carbon (*0.2% C*) steel with sodium chloride led to partial graphitization, a decrease in the amount of nonmetallic inclusions and an increase of mechanical properties.

Derivatographic analyses revealed (Fig.7) that an endothermic reaction occurs in iron at *160–180°C* when adding sodium bicarbonate. It can be explained by the conversion of bicarbonate to carbonate. Sodium

carbonate has a melting point of *851°C*, so a liquid phase forms during sintering, which helps accelerate diffusion processes in powder steel, spheroidization of pores and provides volumetric shrinkages. Water vapor, resulting from the conversion of sodium bicarbonate to carbonate, leads to the oxidation of the surfaces of iron particles.

Polydiethylene glycol adipate   Polypropylene glycol adipate

Polypropylene glycol succinate   Polypropylene glycol sebacinate

Pencil graphite   Pencil graphite with
1 % polypropylene glycol succinate
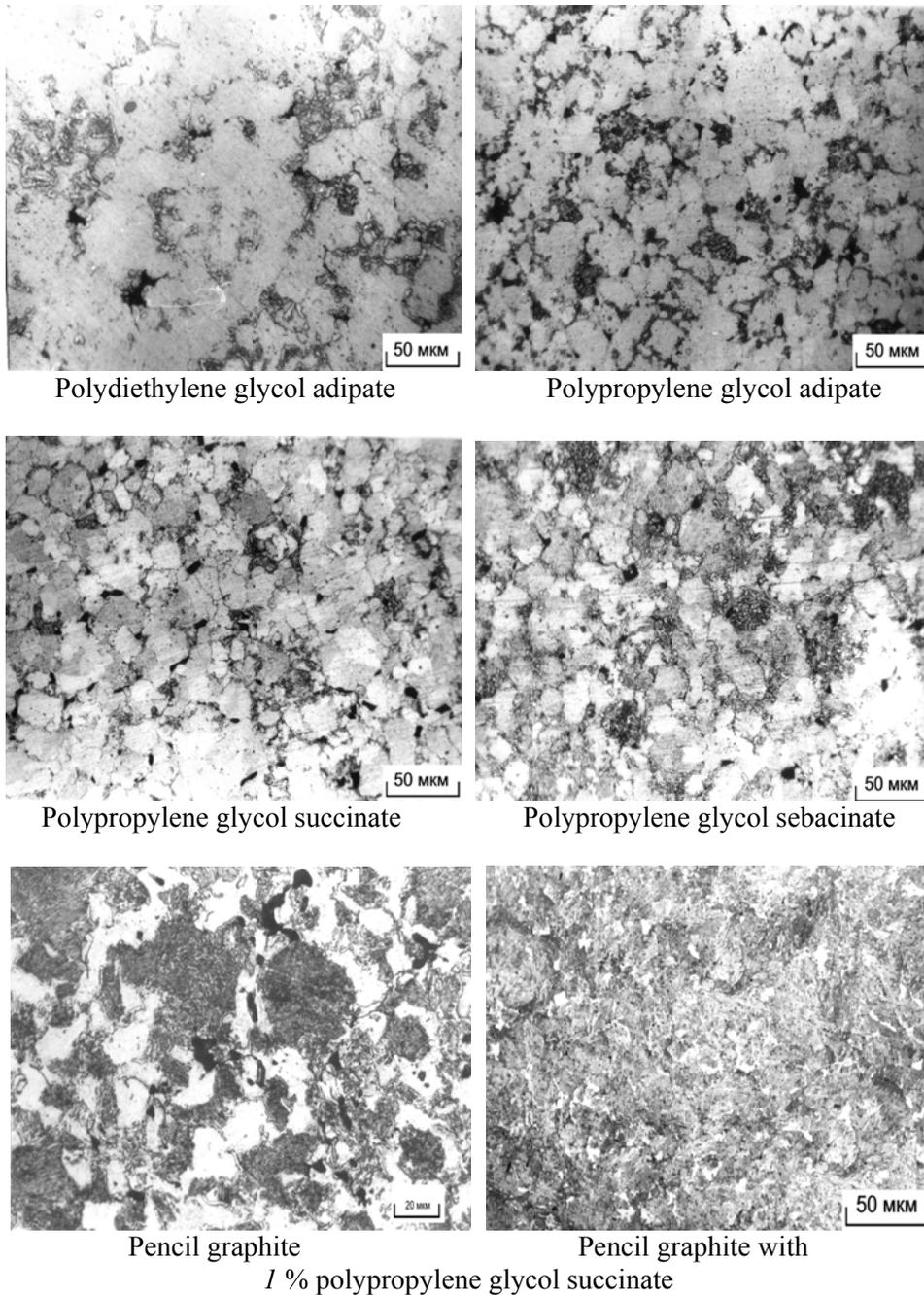
Fig.5. Microstructure of iron with *1%* carbon addition sintered at *1100°C* in endothermic gas.

Oxide films with an increase of sintering temperature are actively reduced under the effect of a reducing atmosphere when sintering. At the same time, self-diffusion of iron atoms and carbon atoms in iron are accelerated. Internal oxidation, which occurs in the early stages of sintering, further enhances the sintering process due to the formation of atomic carbon. When temperature exceeds *700°C*, the thermal

dissociation of carbonate is possible with the formation of sodium oxide and carbon dioxide, which, in turn, interact with graphite to form an atomic carbon

$$Na_2CO_3 = Na_2O + CO_2. \qquad (3.1)$$

Thus, sodium bicarbonate contributes to the self-generation of a carburizing atmosphere. This helps to reduce the decarburization degree of steel by *25–30*% and increase its microhardness from HV 210–240 to HV 270–300.
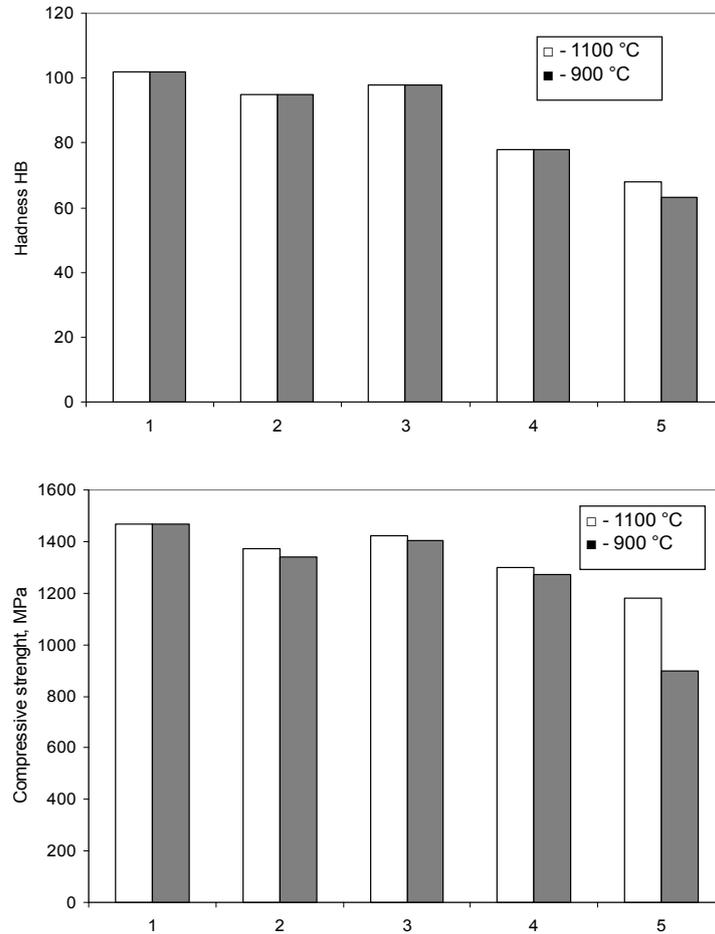
Fig.6. Effects of sintering temperature and type of additive on the hardness and strength of sintered iron:
1 – polydiethylene glycol adipate; 2 – polypropylene glycol adipate; 3 – polypropylene glycol succinate; 4 – polypropylene glycol sebacinate; 5 – zinc stearate.

Two mutually exclusive factors influence the structure formation during sintering of powder steel with the addition of sodium bicarbonate: on the one hand, gas evolution because of decomposition of sodium bicarbonate, and on the other hand, the activation of mass transfer due to the formation of a liquid phase, internal oxidation and the formation of atomic active carbon occurred at the early stages of sintering. One of these effects dominates depending on the amount of sodium bicarbonate introduced. With a large amount (more than *1*%) of sodium bicarbonate, loosening and breaking of contacts in powder samples occurs due to strong gas evolution.

The activating effect of alkali metal compounds on the dissolution of graphite is confirmed by the results of radioactive analyses performed on samples produced of iron powder and iron powder with the addition of sodium bicarbonate. The calculated values of the diffusion coefficients are presented in Tab.2.
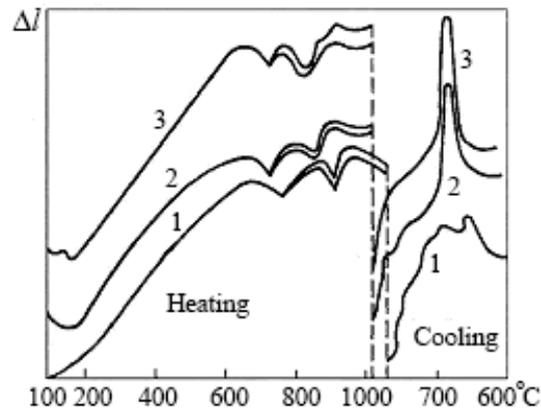
Fig.7. The derivatogram of powder carbon steel: 1 – without additives; 2 – with the addition of 0.2% sodium bicarbonate; 3 – with the addition of 0.5% sodium bicarbonate.

Table 2. Diffusion coefficients of carbon in powder iron.

Material	Carbon diffusion coefficient at various temperatures, $10^7 sm^2/s$			
	950°C	*1000°C*	*1050°C*	*1100°C*
Fe	*2.26*	*4.36*	*5.75*	*11.4*
Fe+0.2% NaHCO$_3$	*4.0*	*6.61*	*10.7*	*13.8*

As it can be seen in Tab.2, the coefficient of carbon diffusion with the introduction of sodium bicarbonate at temperatures of *900–1050 °C* is 1.5–2 times greater in comparison with iron powder. Due to the activating effect on diffusion processes, with the introduction of sodium bicarbonate, pearlite is formed at a lower temperature, the material structure is more uniform and the compressive strength increases by 250–350 MPa.

Conclusions

1 The thermally split graphite obtained by pyrolysis of layered graphite compounds with $FeCl_3$ or $CoCl_2$ compounds provides a homogeneous structure and increases the compressive strength by 80–170 MPa already at a sintering temperature of *900°C* due to the formation of atomic carbon upon decomposition of TSG when sintering.
2 The introduction of macromolecular compounds promotes the acceleration of diffusion processes due to the reduction of oxide films at the boundaries of iron particles, the formation of a pure metal contact and atomic carbon, which makes it possible to obtain a homogeneous structure at a sintering temperature of *100–200°C* lower than that traditionally used for sintering of powder carbon steels. The most effective additives are polypropylene glycol adipate and polypropylene glycol succinate. The introduction of macromolecular compounds improves the compressibility of iron.
3. Sodium bicarbonate has an activating effect when sintering powder carbon steels. The formation of a liquid phase during the melting of sodium carbonate at temperatures above *850°C* promotes pore spheroidization. Additionally, water vapor, resulting from the conversion of bicarbonate to sodium carbonate, leads to the oxidation of the surfaces of iron particles. With an increase of sintering temperature oxide films are actively reduced under the effect of a reducing atmosphere when sintering. The coefficient of carbon diffusion into iron is 1.5–2 times greater when introducing sodium bicarbonate at temperatures of *900–1050°C*.

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