THE ROLE OF CARBONATE ADDITIVE TYPES FOR STRUCTURE FORMATION IN Fe-13Mn-1C PM STEEL

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Abstract
There are two major problems connected with sintering of manganese steels: the high manganese affinity to oxygen and the high Mn vapour partial pressure. It is to be mentioned that inhomogeneous structure is obtained in the case of using Mn powder or master alloys as manganese donor. The conventional way to avoid these negative features of Mn is high temperature sintering (>1473 K) under strongly controlled atmosphere with low oxygen potential. Special care is required to prevent samples from manganese loss at these high temperatures.
The object of this investigation is the examination of possibilities to reduce the temperature and duration of manganese PM steels sintering by using activating (promoting) additives. The influence of two carbonate additives (Na$_2$CO$_3$ and BaCO$_3$) on structure formation in Fe-13Mn-1C PM steel is investigated. The efficiency of additives was estimated by quantitative metallographic analysis. The obtained kinetic dependencies in the temperature range 1123-1423 K show the promoting influence of additives on the structure formation processes.

Keywords: activated sintering, activating additives, sodium carbonate, barium carbonate, manganese PM steel

INTRODUCTION
At the present stage, low manganese alloyed PM steels (1-4% Mn) are being investigated and produced [1-13 etc.]. Usually atmospheres with low oxygen potential are used, including vacuum, as well as high sintering temperatures. The sintering temperature is recommended to be 1473-1553 K in order to ensure the accomplishment of densification and homogenisation. In spite of the high temperatures, homogeneous microstructure is usually not observed in the sintered material. Even liquid-phase sintering leads to non-homogeneity expressed predominantly in separation of carbide nets on the grain boundaries. For these reasons implementation of additional heat treatment is required. The fact that at high temperature sintering despite the manganese-containing getter, the probability of having manganese loss processes is too high and could not be disregarded. Along with this it should be noted that the strict control of the gas atmosphere, high temperature sintering and additional heat treatment complicate, and to a great extent, raise the cost of producing PM manganese alloyed steels. Therefore, considering the possibilities for sintering manganese alloyed PM steels at lower temperatures, and for a shorter time but without deteriorating their quality, would decrease the risk of oxidation and manganese loss and simultaneously would decrease the production cost. The solution of this problem has a great practical and theoretical significance. Moreover, development of technologies for Mn applications in a wide range of concentration is very topical because it is a challenging substitute for the potentially carcinogenic nickel. On the other hand, high manganese PM
steels could be used for production of small wear resistant parts or details with austenitic microstructure for the electrical industry.

One of the promising routes to achieve the task set is activated sintering and more concretely – the use of promoting additives. Depending on the mechanisms of activating the sintering process, they could be divided in several groups. For instance, the addition of elements or chemical compounds forming liquid phase is widely applied [14-16]. Good results are obtained when the sintering process is accompanied by simultaneously running a reducing process. An oxide of sintered metal is used as an activator in this case [16,17]. Chemical compounds are used as activators, which generate the gaseous phase - carrier of alloying element [18,19].

The aim of the submitted work is investigation of the possibility for sintering high manganese PM steel at a lower temperature and for a shorter time. To this end, the role of Na$_2$CO$_3$ and BaCO$_3$ for the structure formation process in Fe-13%Mn-1%C PM alloy is examined. There are published data about these types of additives for their activating influence upon the sintering processes of double Fe-C PM systems, as well as on triple systems of the type Fe-Me-C [21]. However, their applicability for activated sintering of triple Fe-Mn-C PM alloys was not investigated.

EXPERIMENTAL PROCEDURE

Samples and sintering

Iron powder NC 100.24 (Höganäs) was used. Milled ferromanganese was used as a manganese donor, produced in the metallurgical combine “Kremikovsky”, Bulgaria (79.35% Mn, 1.92% C, 0.548% O$_2$ and average particle size on Fisher – 16.2 μm). Graphite pencil brand 3KB (GOST 4406) was used. Sodium carbonate and barium carbonate were used as additives, Fluka (P.A). The quantity of carbonates added was 0.50% and it was established in previous investigations [8]. Samples $\varnothing$15x3 mm of green density 6.50 g/cm$^3$ were pressed for the purpose of the investigation. The sintering was carried out in vacuum furnace at 10$^{-4}$ MPa. The use of vacuum eliminated the furnace atmosphere influence on sintering processes. The specimens were heated and cooled together with the furnace. Average rate of heating/cooling was 5 K/min. Samples were sintered in ceramic crucibles with a lid, packed in fine Al$_2$O$_3$ and ferromanganese. Sintering was carried out for 5, 10, 15, 30, 60 and 90 minutes at each temperature (1123, 1173, 1223, 1323 and 1423 K).

Estimation of structure formation process

Kinetic dependence was determined by means of quantitative metallographic analysis of the sintered samples. It was performed by linear method [23]. Absolute error varies from ±1.53 up to ± 4.47 vol.% depending on the correlation between the phase (or the structure components) quantities (from 3:97 to 50:50 vol.%, respectively). Due to the very dynamic structural changes during sintering, step-by-step quantitative evaluation of two characteristics describing the structure formation rate was carried out. The summary structural changes were determined by the first characteristic without concerning the nature of the phases formed. The difference to 100% vol. is ferrite, which had not undergone structural changes. The second characteristic specifies the quantity of pearlite (sorbite, troostite). The difference between the first and second feature gives the structural changes because of the double alloying of the iron matrix with C and Mn (bainite, martensite and austenite). These structural changes are determined only qualitatively.
RESULTS AND DISCUSSION

The observations carried out on the process of microstructure formation in Fe-13Mn-1C PM system show that the mechanism of the microstructure formation does not depend on the presence of the additives, but they considerably affect the process kinetics.

Despite the sintering temperature, saturation of the iron matrix with alloying elements begins with their diffusion along the particle surfaces and grain boundaries. With an increase of sintering duration, a subsequent penetration of the two elements in the volume of the particles and grains is observed. This succession of alloying is determined by the great difference in rate of the surface and volumetric diffusion. On the other hand, since the diffusion coefficient of carbon considerably exceeds that of manganese, processes of alloying the iron matrix begin with carbon diffusion [24, 25]. As a result the areas enriched mainly with carbon are usually situated nearer to the centre of the particles (grains). Closer to the particle periphery there are areas enriched with both alloying elements (C and Mn). After sintering, a typical ring shape microstructure is formed. It is present not only in the high manganese alloy (13% Mn) as in this case, but also at lower manganese contents (for example: 5, 6, 10, 11, 12) particularly with the short sintering times [12]. This type of microstructure is due to the already mentioned different degree of alloying with Mn and C of the particle peripheral and central zones. The complete sequence of microstructures from the core to the periphery of the particles is: ferrite - pearlite (sorbite, troostite) obtained by hypoeutectic transformation - martensite (bainite, austenite) - troostite (ferrite-carbide mixture) as a result of initial carbides separation from hypereutectic alloy - martensite - carbide net. This succession changes dynamically depending on the sintering temperature and time and it is often not fully completed. The structure features are determined by quantitative correlation between carbon and manganese in every point of the sample. In the presence of additives these differences are retained.

Fig. 1. Microstructure of samples sintered at 1123 K, 90 min (a – sample without additive, b- sample with 0.50% Na$_2$CO$_3$, c – sample with 0.50% BaCO$_3$: 1- troostite ring, 2 – martensite ring, 3 – diffusive porosity in ferromanganese particle).
In samples sintered at 1123 K the structure formation begins with formation of troostite sections close to the surfaces of the initial powder particles. In the samples without additives layers of troostite and mixed layers of troostite and carbide net are observed (Figs.1a, 2a).

Fig.2. Structural changes in PM alloy Fe-13%Mn-1%C after sintering at different temperatures (B0, BA, BB – summary changes, B-p, BA-p, BB-p – pearlite).
The beginning of slight manganese diffusion into the ferrous matrix is observed. This process is manifested by diffusive porosity in some ferromanganese particles.

Increasing the temperature by 50 K, mainly results in more intensive formation of phases of pearlite type (Fig.2b). Its quantity intensively grows up to 15 min and more slightly up to 30 min sintering. A further increase of the sintering duration does not lead to significant changes in this quantity.

After sintering at 1123 K in the presence of Na$_2$CO$_3$ an increase of the rate of running of these processes is observed (Fig.2a, $\tau > 60$ min). After 90 min sintering a thin martensite ring is observed (Fig.1b). After sintering at 1173 K the pearlite participation in the summary structure changes is less than in the samples without additives (Fig.2b, $\tau > 60$ min). It is due to an increase of the rate as well as to the quantity of complex alloyed structures (bainite, martensite, austenite). Barium carbonate retards microstructure formation in the temperature range of 1123-1223 K. The results for the mentioned temperature range coincide with the data pointed out in [19] and contradict the results of [20]. Since in [19] investigations are performed in atmosphere of inert gas, in [20] - in a stream of cracked ammonia and the present - in vacuum, unified conditions of the experiment could not be discussed.

It should be noted that the respective activating additive alone provokes accelerated carbon diffusion only in the initial sintering period. Its duration depends on the temperature and has not a clearly defined limit. After this initial stage, alongside the effect of the promoting additive presence there is added the joint carbon and manganese influence upon their solubility in iron [24]. The mutually accelerating influence continues to the moment when formation of the combined carbide phase begins. Carbide formation in the manganese and carbon alloyed matrix begins more rapidly because they jointly change the position of p.S of the Fe-Mn-C equilibrium phase diagram. They draw it to lower carbon contents and lower temperatures. Combining both elements in carbide ((Fe,Mn)$_3$C) reduces their activity and the diffusion rate decreases.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Samples</th>
<th>Average microhardness HV0.050 of ferrite after sintering for time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1123</td>
<td>B0</td>
<td>147 135 176 186 200 191</td>
</tr>
<tr>
<td></td>
<td>BA</td>
<td>153 168 192 177 177 207</td>
</tr>
<tr>
<td></td>
<td>BB</td>
<td>100 166 150 149 125 181</td>
</tr>
<tr>
<td>1173</td>
<td>B0</td>
<td>131 195 148 185 216 239</td>
</tr>
<tr>
<td></td>
<td>BA</td>
<td>119 224 207 212 120 251</td>
</tr>
<tr>
<td></td>
<td>BB</td>
<td>106 175 121 170 183 251</td>
</tr>
</tbody>
</table>

This on its part provokes the beginning of “ascending diffusion” from the alloyed ferrite matrix to the areas of intensive carbide formation. The next penetration of Mn and C to the core of the particles depends on the dynamic correlation between the concentrations of both elements. As an example Table 1 shows the dependence of phase microhardness (ferrite) on the sintering time at 1123 and 1173 K and on the introduced additive. Its value is determined by the extent of the ferrite matrix alloying. The decrease of the microhardness (Tab.1, grey cells) of the base simultaneously or immediately after the increase of the
quantity of pearlite formed attests for the participation of alloying elements in the carbide formation processes. Pearlite microhardness in these cases varies around 300-400 HV0.05.

Quantitative correlation among the phases formed after sintering at temperatures 1223, 1323 K are given in Fig.2c,d. In the samples without additives the bulk of structural changes at 1223 and 1323 K are because of the pearlite formed. A typical ring-shaped structure is formed. The microstructure of the complex alloyed areas represents the martensite edge surrounding troostite fields. With increasing the holding time, depending on the temperature, the troostite is replaced either by troostite + bainite or by martensite. The character of microstructure formed in the presence of carbonate additives at the same temperatures attests for accelerated diffusion of carbon and manganese. Besides the fine pearlite structure at earlier stages a mixed structure is formed by troostite, bainite and martensite. With increase of the sintering duration the summary structural changes envelop more and more of a great part of the surface observed and the participation of pearlite type structures in them decreases. Appearance of two pearlite maximums is observed. The first of them is due to mainly hypoeutectic transformation. The second maximum is summary result of hypoeutectic transformation and the obtaining of hypereutectic ferrite-carbide structure due to lowered austenite stability as a result of initial carbide separation. It is registered at 1223 K for samples with Na$_2$CO$_3$ and at 1323 K for those with BaCO$_3$ and without additives. Moreover, in comparison with the samples without additives, in the samples with promoting additives the pearlite formation is drawn to shorter sintering times and its quantity is less (Fig.2 c, d). The qualitative composition of the complex alloyed structure components is different as well. Martensite and austenite are predominant. Diminishing of microhardness is observed as a result of the increased quantity of retained and undercooled austenite and the decreased martensite quantity.

After sintering at temperature 1423 K the quantitative structural changes have different character from these at 1223 and 1323 K (Fig.3). For short sintering time, formation of higher quantities of ferrite-carbide structure is observed in samples with additives than in the sample without additives (Fig.2 e). This structural constituent appears as an edge on the formed, in the progress of the process, bainite, martensite and austenite.

Having in mind the diffusion direction from periphery of the particles to their centre and the Fe-Mn-C equilibrium phase diagram, it could be said that these zones have hypereutectic composition. After 60-90 min sintering at this temperature the structure is composed as follows:

In the samples without additives - bainite, martensite and retained austenite (789 HV0.05), ferrite-carbide mixture and carbide net on the grain boundaries. With Na$_2$CO$_3$ additive - predominant martensite - there is austenite structure (990 HV0.05) with separate ring-shaped ferrite-carbide sections and carbide net on the grain boundaries. With BaCO$_3$ - analogous structure to the one obtained with the addition of sodium carbonate. Average microhardness of martensite and retained austenite 831 HV0.05.

On the basis of observations carried out, it could be maintained that both types of carbonate additives accelerate the process of structure formation. Their influence upon the kinetics of structure formation is due to a sophisticated complex of reasons.

In [24,25] a mechanism is proposed for the activating action of the carbonate additives. It is based either on initial thermal decomposition of the carbonates or on interaction between carbonate and carbon as a result of which CO$_2$ is obtained. With its appearance, the running of a cycle of reactions is provoked. The basic reaction is its interaction with C(gr) and production of CO. The CO decomposition on the iron surface and the production of active carbon atoms is the main reason for the accelerated structure formation. The obtained CO$_2$ regenerates MeO to MeCO$_3$. Low-melted Na$_2$CO$_3$ as a liquid
phase takes part in the refining of the metal surface, which also favours the process. In author’s opinion, of essential importance as to the different temperature of beginning the activating effect is the thermal stability and the dissociation pressure of the investigated carbonates.

![Fig.3. Microstructure of samples B(a,b), BA (c,d) and BB (e,f) after sintering at 1423 K for 5 min (a,c,e) and 90 min (b,d,f).](image)

It is known that BaCO$_3$ possesses higher thermal stability than Na$_2$CO$_3$ but its dissociation pressure in the temperature range 1290-1430 K is considerably higher (about 10 to $10^2$ times) than that of the sodium carbonate [26].

**CONCLUSIONS**

- Additives of sodium and barium carbonate accelerate the microstructure formation process in Fe-13Mn-1C PM alloy.
- Carbonates begin to activate the process at different temperatures: Na$_2$CO$_3$ - at 1123 K, BaCO$_3$ - at 1323 K.
- The type of the additive by which to control the process of structure formation may be chosen with dependence on the purposes.
Acknowledgments

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