MANGANESE GAS-PHASE ALLOYING OF SINTERED STEELS ANALYSED BY DILATOMETRY: EFFECT OF CARBON, BASE POWDERS AND MANGANESE CARRIER

M. Selecká, A. Šalak

Abstract
Dilatometer tests of mixed Fe-Mn-(C) and hybrid Fe-Mo-Mn-(C) and Fe-Cr-Mo-V-Mn steels at 1150°C in H\textsubscript{2}/N\textsubscript{2} atmosphere with a dew point of -30°C were performed. The effect of manganese and carbon content and manganese carrier on the manganese gas-phase alloying of the tested materials was demonstrated by swelling and shrinkage in dilatometer graphs. The measurable start of the swelling of the specimens caused by manganese sublimation was determined at about 600°C. The specimens attained the maximum swelling after aborting the preheating period; higher manganese and carbon content resulted in higher swelling. The various effects of sponge and atomized iron powder and of manganese carrier grades were recorded. Shrinkage of the Mn steel specimens during isothermal sintering, caused by demanganisation expressed in manganese loss and by enhancing effect of manganese for sintering, was recorded. The final dimensional changes of Mn steel samples do not characterize the individual manganese steels because of lower final manganese content due to demanganisation.

Keywords: sintered structural steel, dilatometry, manganese, demanganisation, microanalysis, dimensional change

INTRODUCTION
Manganese could be an attractive alloying element in powder metallurgy as the cheapest alloying element, and due to its high hardening effect. Manganese alloyed sintered steels have been investigated quite frequently but up to the present time large scale production of Mn alloyed sintered parts has not been established. The reason for this situation is still regarded as the high affinity of manganese for oxygen – the hard reducibility of its oxides. The thermodynamic requirements for purity of the sintering H\textsubscript{2}/H\textsubscript{2}O atmosphere for reduction of manganese oxides expected on particles of the manganese carrier in a compact would be not possible to meet. This requirement has to be orientated especially in industrial sintering on the preheating zone, which is an entry lock for the parts, as well as the dewaxing zone. Sintering of manganese containing steels is in reality based on a physical property of manganese - high vapour pressure. The consequence of it during sintering is manganese sublimation from the Mn carrier particles expressed as a self-cleaning (protection, reduction) effect of manganese for sintering atmosphere though which occurs as an effective solid phase - gas phase sintering process of manganese steels [1,2].

The dilatometer tests on PM materials were performed for the characterization of the behaviour of the compacts during sintering, and mainly of the dimensional changes, which are crucial for the dimensional stability. This was the reason for dilatometer testing also of Fe-Mn-C steels involving many actual factors showing, i.e. the following data.
From this point of view the Fe-4% Mn, Fe-2% Si and Fe-2% Si-(2,4)% Mn steels for 3 h at 1180°C in dry hydrogen were tested [3]. The Fe-6% Mn steel samples based on ASC 100.29 powder were tested for (0 - 300) min at 1160°C in pure hydrogen [4]. Similarly the Fe-(3,4)% Mn-0.8% C steels based on NC 100.24 powder were tested for 1 h at 1120, 1240 and 1300°C in hydrogen (dew point -60°C) [5]. The Fe-(0,2,4)% Mn-0.3% C steels based on ASC 100.29 powder were tested for 60 min at 1275°C in vacuum [6].

The object of this work was complex analysis of the course of the dimensional changes of manganese containing steels recorded in dilatometer curves during sintering in relation to the manganese and carbon content, manganese carrier, and base iron and prealloyed powder grades.

EXPERIMENTAL PROCEDURE

For the preparation of specimens for the dilatometer tests, the following base powders were used:

- iron powder: SC 100.26 and ASC 100.29; prealloyed powders: Astaloy 85Mo (Ast85Mo), Astaloy Mo (AstMo) (all Höganäs AB) and Fe-1Cr-0.3Mo-0.3V (103CRV, Kawasaki),
- manganese carriers:
  a) electrolytic manganese (99.8%, 0.63% O, particle size <20 μm, supplied as-milled by GfN Nuremberg) coded here EMn,
  b) medium carbon ferromanganese (80% Mn, 1.1% C, 0.67% O; particle size <45 μm, ERATEM Sauda) coded here FeMn,
  c) high carbon ferromanganese (76% Mn, 6.6% C, 0.77% O; particle size <45 μm, OFZ Istebné) coded here FeMnC;
- natural graphite CR 12 (Grafit a.s. Netolice).

Both ferromanganese grades were milled in a ball mill in nitrogen; the oxygen content after milling in air was higher by 0.3-05%.

The surface of as-milled manganese carrier particles, independently on milling atmosphere, was covered by a dark grey film – a product of the wear between the milled manganese carrier and cast milling balls (MnO₂ by X-ray analysis on the surface of manganese carrier powders was detected only).

The powder mixtures were compacted into the specimens in a size 4 x 4 x 15 mm. The resulting green densities of the specimens were ~6.6 g/cm³. Sintering was carried out in a horizontal push rod dilatometer NETZSCH 402E (AGH Krakow) under the conditions listed in captions. The evaluation of dilatometer graphs was particularized by microanalysis of manganese concentrations and microhardness measurement in sintered microstructures, and by the apparent hardness and transverse rupture strength determination of the final Fe-Mn-(C) specimens.

Tab.1. Starting characteristics of the tested powder Fe-Mn-C steels.

<table>
<thead>
<tr>
<th>Steel No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn added [%]</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Mn carrier</td>
<td>FeMn</td>
<td>FeMnC</td>
<td>FeMn</td>
<td>EMn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C mass [%]</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>*0.16</td>
<td>*0.24</td>
<td>*0.40</td>
<td>0.20</td>
<td>0.50</td>
<td>0.90</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Iron powder</td>
<td>SC 100.26</td>
<td>ASC 100.29</td>
<td></td>
<td>SC 100.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Remark: *C<sub>c</sub> combined as FeMnC, C in steels No. 11-13 as graphite. Plain iron powder specimen - Fe(0)
RESULTS AND DISCUSSION

Effect of manganese

Figure 1 shows the dilatometer graphs for Fe and Fe-(2-5)Mn steel specimens. The increasing linear swelling (expansion) with increasing temperature and manganese content was characteristic for all specimens compared to plain iron specimen as presented also in [4-6].

The expansion of Mn containing specimens was larger compared to the expansion of the Fe specimen. There was formed a larger difference in expansion between the Mn containing and Fe specimen, and lower only between the Mn specimens in dependence on Mn content added. This is clearly marked in the graphs at 600°C as a total expansion of 0.3% for 5Mn steel. It is possible to assume that the beginning expansion of Mn specimens up to 600-700°C was caused mainly by the thermal expansion of FeMn particles in the compacts. Contemporary in this temperature range, the manganese vapour formation by sublimation from FeMn particles could be demonstrated and its condensation on the surface of the iron particles in the compact. The temperature of ~700°C was before regarded for that at which, by optical microscopy, was observed the manganese gas-phase alloying of iron powder particles in the compacts [1]. It is necessary to note that at the temperature of 400°C, at which manganese starts to oxidize, no changes on the dilatometer graphs were observed.

Fig.1. Dilatometer curves for Fe(0) and Fe-(2,3,4,5)Mn specimens and temperature-time profile. Isothermal sintering for 30 min at 1150°C, 75H₂/25N₂ atmosphere, dew point -30°C, heating rate 10°C/min, cooling rate 30°C/min [7].
The dimensional changes of Fe-Mn specimens in α-γ transformation temperature range were also the demonstration of an alloying of the iron matrix by manganese (the decrease of the phase transformation temperature by Mn addition compared to that of plain iron compact). The increasing temperature in γ-region demonstrated in further increased swelling of the Fe-Mn specimen’s length with larger differences with increasing Mn content due to larger through alloying of individual iron particles in austenite. The samples attained higher swelling by ~0.7% compared to Fe(0) sample with a completed preheating period at 1150°C. This process occurred as solid state (iron powder) - gas phase (Mn vapour) alloying of sintered Mn steels [8,9]. The dimensional changes on the graphs show that the heating period is the most important stage of sintering and alloying of iron matrix by manganese.

The graphs proved the progressive alloying of the iron powder matrix with manganese in an H₂/N₂ atmosphere with the dew point of -30°C, which did not correspond to the requirements of Ellingham - Richardson diagram. According to this for elimination of the manganese oxidation, the sintering atmosphere, i.e. at 600°C, should have the dew point -102°C [2] regarding also that manganese starts to oxidize at 400°C [8]. The manganese vapour formation by sublimation from the ferromanganese particles is the consequence as mentioned previously of a physical property of manganese - high manganese vapour pressure [9-11]. This is much higher than that of other alloy elements used in PM as, e.g. at 600°C of Mn is 2.88x10⁻⁵ Pa, at 700°C 1.33x10⁻³ Pa, at 800°C 2.95x10⁻² Pa and at 900°C of Mn is 3.8x10⁻¹ Pa and, i.e. of Ni is 3.95x10⁻⁶ Pa. This contrast in vapour pressure of Mn and Ni retains also at 1200°C which for Mn is 98.69 Pa and for Ni 2.68x10⁻³ Pa [12]. Manganese vapour condensed uniformly on the surfaces of iron powder particles in the compact, and from here manganese diffused into their cores by basic diffusion mechanisms (volume, grain boundary, and pipe) and by diffusion grain boundary migration (DIGM) [13]. The expansion of the dimensions of the “green” Fe-Mn compact even in the early preheating sintering period was the effect alloying by manganese. The compacts started to behave as “Fe-xMn” alloys.

The characteristic shrinkage of the Fe-Mn specimen’s length was recorded on the dilatometer graphs during the isothermal sintering, compared to the constant dimension of Fe(0) specimen. This was shown also in previously published works [3-6], but without an analysis. This appearance can be explained by a reverse sublimation of manganese from the by manganese alloyed specimens, i.e. demanganisation characterized by manganese loss in the sintered compacts. This was again the effect of high manganese vapour pressure which is 19.88 Pa at 1100°C [11]. The same decrease of the expansion of hybrid Fe-Mn-Cr-Mo-C steel sample length at the dilatometry tests was observed during holding time at 1120°C and 1250°C in the atmospheres of different composition by dilatometry tests [14]. In sintered state there was formed a relative “high” concentration gradient in Mn between the Fe-Mn sintered specimens and the surrounding atmosphere causing this unavoidable process. The demanganisation of the samples was also demonstrated in the course of the cooling part of the graphs without a marked dimensional change at expected γ-α phase transformation temperature compared to the iron specimen graph. Consequently, according to this first assumed knowledge, the final as-sintered manganese content in the specimens, due to demanganisation, will be lower than the starting added one. The final dimensional change of the manganese containing steel specimens recorded by the dilatometry cannot be therefore accepted as representative for the specific sintered Mn alloy steel.
Effect of iron powder grades

The effect of the iron powder grades used was demonstrated also in graphs in relation to the manganese content clearly in the highest swelling values of the specimens at the begin of isothermal sintering at 1150°C as shown in Fig.2.

![Dilatometer graphs for Fe-(2,3,5)Mn steels based on: SC 100.26 (steels No.1, 2, 4, Table 1) and ASC 100.29 (steels No.5, 6, 7, Table 1) iron powder. Mn added as FeMn. Isothermal sintering for 60 min at 1150°C, 75H/25N atmosphere, dew point -30°C, heating rate 10°C/min, cooling rate 15°C/min [7].](image)

The Fe-2Mn specimen based on ASC iron powder exhibited larger swelling compared to that based on SC iron powder, and conversely the Fe-3Mn specimens. According to [15], the Fe-8Cu steel based on water atomized iron powder exhibited in dilatometry test at 1120°C an expansion of 3.3% compared to that based on sponge iron powder (0.7%) which proves in some range, in relation to the tested material system, the attained results. The effect of iron powder grade did not demonstrate more in the graphs for 5Mn specimens due to more homogeneous through alloying of the matrix by manganese. It follows from this that a different course of alloying by manganese of these powder grade particles occurred during preheating. This is caused by their different physical-metallurgical characteristics given by the production method [16] (particle size distribution, specific surface area, grain size, chemical impurity and lattice imperfections) affecting the diffusion process by manganese. The shown differences in the graphs caused by the iron powder grades recorded at 1150°C were retained without significant changes during isothermal sintering shrinkage, and as well as during cooling. The more marked final differences in dimensional change between the individual steel specimens in relation to the Mn content and iron powder grade compared to that shown in Fig.1, as assumed by the authors, were caused by longer isothermal sintering time (60 min), in that case demonstrated in more homogeneous alloying of the matrix by manganese.

Effect of carbon

In Figure 3 are shown the dilatometer curves of sintered iron and Fe-(2,3,5)Mn-(0.16,0.24,0.40)C and of Fe-3Mn-(0.2,0.5,0.9)C steel specimens characterized by various manganese and carbon contents.
Fig. 3. Dilatometer curves for: left - Fe-(2,3,5)Mn-(0.16,0.24,0.40)C steels (steel No. 8-10, Table 1), right - Fe-3Mn-(0.2,0.5,0.9)C steels (steel No. 11-13, Table 1) [7]. Processing as in Fig. 2.

The mentioned differences in base material characteristics were demonstrated clearly by swelling in \( \gamma \) - region up to 1150°C of both steel groups. The effect of carbon addition was demonstrated markedly in both cases by increased swelling of the dimensions over the \( \alpha \) - \( \gamma \) transformation temperature up to 1150°C compared to the carbonless specimens shown in Figs. 1, 2, due to the dissolution of carbon in austenite. The different effect of combined and free carbon addition on dimensional changes shows the graphs as follows from the comparison of swelling of Fe-3Mn-0.24C and of Fe-3Mn-0.5C steels. On the other side, the Fe-5Mn-0.4C steel was exhibited by the same swelling of the dimension as the Fe-3Mn-0.9C steel (3.9%). The results can be affected also by larger decarburization of the of Fe-3Mn-graphite samples during the isothermal sintering apart from the demanganisation, compared to those alloyed with combined carbon content. The graphs of both groups retained the same character also during the cooling period. The addition of carbon according to Fig. 3a, markedly emphasized in the cooling part of the graphs the differences in effect of the starting manganese addition.

The shown differences in dimensional expansion of these steels were the consequence of uneven diffusion activity of added manganese and carbon. In the first case manganese and carbon were added as combined (FeMnC) and in the second case as free carbon (graphite) and medium carbon ferromanganese (FeMn). Contrary according to [15], at 1120°C an expansion of \( \sim 1.5% \) was recorded for Fe-8Cu-0.8C compared to that for Fe-8Cu steel of \( \sim 3.3\% \).

Effect of manganese carrier

The testing of the effect of medium ferromanganese and electrolytic manganese as manganese carriers on alloying of sintered steels including previous results has a scientific-technical and economical significance; the ferromanganese grades are the cheapest industrial manganese carriers and on the other hand the electrolytic manganese is the cleanest one, but more expensive.

The curves in Fig. 4 show clearly a varied effect of EMn and of FeMn on swelling of the dimension of 2Mn steels compared to 4Mn steels (state at 1150°C). The Fe-2Mn steel alloyed with FeMn exhibited lower swelling than that alloyed with EMn. On the contrary, the Fe-4Mn steel alloyed with EMn exhibited the same swelling as the Fe-2Mn steel, and during the isothermal sintering, shrinkage at the lowest value between the
investigated steels occurred. The curves retain then the same character during the cooling period.

![Graph](image)

Fig.4. Dilatometer graphs for Fe-(2,4)Mn steels based on SC 100.26 iron powder alloyed with: FeMn (steels No. 1, 3, Table 1) and EMn (steels No. 14, 15, Table 1). Processing as in Fig.2.

The differences between both manganese carriers consisted in particle size, and in chemical activity (ferromanganese - lower chemical activity). It is possible to deduce that the cause of this appearance lies in the fineness of EMn particles used (-20 μm), and in its higher chemical activity. The time of full manganese sublimation from one EMn particle size 15 μm at 600°C is $5.7 \cdot 10^{3}$ s and at 700°C is $1.3 \cdot 10^{3}$ s [11]. Under such conditions, the sublimation of manganese from all EMn particles followed by condensation on the iron particles occurred relatively fast in early preheating stages. It means the reverse sublimation of manganese from the specimens could start even during preheating. This was demonstrated in such case in lower swelling during preheating and in the final small differences in the course of graphs between the 2Mn and 4Mn steels. The use of electrolytic manganese as the manganese carrier for alloying of sintered manganese steels needs to be investigated in more detail.

The difference in chemical activity expressed in manganese mass loss between the finer EMn and coarser FeMnC particles processed at various “sintering” temperatures in dependence on holding time is shown in Fig.5. The initial larger manganese loss from FeMnC charge was caused by the decarburization. As shown, the manganese loss from EMn particles at 1200°C during ~60 min reached 85% and 50% from the FeMnC batch. This can be related also for FeMn as confirmation of lower chemical activity at manganese sublimation from ferromanganese powders, compared to EMn as manganese carrier.
Fig. 5. Manganese loss from loose manganese carrier particles at heating in Mars furnace in an oxal boat in high purity hydrogen in dependence on holding time and temperature: left - EMn, mass 0.03 g, specific surface area 0.54 m$^2$/g; right - FeMnC, mass 0.04 g, specific surface area 0.62 m$^2$/g, both particle sizes <20 $\mu$m after milling in air [17,18].

Additional “annealing” tests were performed for evaluation of the effect of the temperature and of the mass of the test batch Mn powders on the manganese loss by sublimation, and the results are listed in Table 2.

Tab. 2. Mass and percentage loss of manganese by sublimation from electrolytic manganese (particle size <20 $\mu$m) at heating for 10 min at 1120°C and 1220°C in a Mars furnace in an oxal boat in high purity hydrogen in relation to the mass of the test batch [17].

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Test batch [g]</td>
<td>Mn loss [g]</td>
</tr>
<tr>
<td>0.03050</td>
<td>0.00300</td>
</tr>
<tr>
<td>0.30725</td>
<td>0.00463</td>
</tr>
<tr>
<td>2.99415</td>
<td>0.01260</td>
</tr>
</tbody>
</table>

The results show an increased manganese loss by sublimation in all cases at increased treating temperature due to higher manganese vapour pressure (higher sublimation rate). On the other hand the manganese loss was at both temperatures decreasing with increasing mass of the test batch of EMn particles. It was the effect of the “thickness” of the test batch; i.e. of the lower mass of the test batch – the thinner layer more particles took part on sublimation compared to that in a thicker layer. There can be deduced a need to secure a maximum homogeneous distribution of Mn particles at mixing with iron powder (elimination of clusters).

**Effect of prealloyed powder grades**

The prealloyed FeMo and FeCrMo(V) powders with an addition of manganese present new hybrid nickel- and copperless high performance sintered steel groups. The aim
of the dilatometer testing was therefore to analyze the course of the manganese gas-phase alloying of prealloyed powder compacts forming these hybrid steels. The following materials, based on prealloyed 1.5Mo (Ast.Mo), Fe-0.85Mo (Ast.85Mo) (both Höganäs AB) and Fe-3Cr-0.3Mo-0.3V (KIP 30CRV, Kawasaki) powders, were tested.

In Figure 6 are shown the dilatometer graphs for prealloyed Fe-0.85Mo (Ast.85Mo) powder compacts with an addition of manganese and carbon sintered at 1200°C.

Fig.6. Dilatometer curves for hybrid Fe-0.85Mo-(0,1,2,3)Mn and Fe-0.85Mo-3Mn-0.25C steel specimens (Mn added as FeMn, C as graphite). Isothermal sintering for 30 min at 1200°C, heating rate 10°C/min, cooling rate 15°C/min, 30H₂/70N₂ atmosphere, dew point -40°C [19].

The graphs also proved an intense gas-phase alloying effect of Mo-prealloyed matrix in relation to the manganese and carbon addition. The effect of manganese addition on dimensional changes of the samples during preheating had the same increasing character with marked changes at α - γ phase transformation temperature as in Fe-Mn systems. (The lower expansion of Fe-0.85Mo specimen compared to iron specimen is necessary to regard at the evaluation). The larger linear expansion in dependence on manganese content compared to Ast.85Mo specimen was determined in the graphs up to 600°C, which can be explained by the thermal expansion of FeMn particles as stated in Fig.1. The linearity of the curves over this temperature was decreasing up to α - γ transformation temperature. This change in expansion of Mn containing specimens could be only the consequence of manganese sublimation and its condensation on base powder particles in the compact. This feature makes a possibility to qualify the temperature of ~600°C for that at which starts the effect of manganese sublimation in 75H₂/25N₂ atmosphere with the dew point -30°C, contrary to 700°C as stated before (determined by optical microscopy).

The effect of 0.25% carbon addition expressed itself in austenite by a relative large increase of swelling compared to the 3Mn steel without carbon. The demanganisation of these samples was demonstrated by the same character of the shrinkage as was stated for the Fe-Mn steels.
Figure 7 shows the dilatometer graphs for the steel with 3% Mn and 0.25% C based on prealloyed Astaloy Mo powder. The linear swelling of the hybrid Fe-1.5Mo-3Mn-0.25C steel, according to the graph, is approximately at the same level at 1150°C as that shown in Fig.6 for Fe-0.85Mo-3Mn-0.5C steel considering in this case lower sintering temperature and carbon content. It is possible to assume the same course of alloying of both 0.85Mo and 1.5Mo prealloyed matrix by manganese including the shrinkage caused by demanganisation.

The graph for hybrid Fe-3Cr-0.3Mo-0.3V-3Mn-0.25C steel shown in Fig.8 differs from that shown in Fig.7 with the same Mn and C content by markedly lower final swelling at 1150°C followed by lower shrinkage. On the contrary, higher swelling exhibited the base matrix compared to Fe-0.85Mo and Fe-1.5Mo matrices, Figs.6,7.

**Microstructure and dimensional change**

The microstructure characterization, microconcentrations of manganese and micro- and macrohardness measurements, and bending strength determination of the specimens based on iron powders for approval of the stated demanganisation was carried out.

![Fig.7. Dilatometer curves for Fe-1.5Mo (AstMo) and hybrid Fe-1.5Mo-3Mn-0.25C (graphite) steels (Mn added as FeMn). Isothermal sintering for 30 min at 1150°C, other as in Fig.1.](image)

![Fig.8. Dilatometer curves for Fe-3Cr-0.3Mo-0.3V-3Mn-0.25C steel samples (Mn added as FeMn, C as graphite). Isothermal sintering for 30 min at 1150°C, other as in Fig.1.](image)

![Fig.9. Microstructures of: a - Fe-2Mn specimen - No.1 (m - margin, c - core); b - Fe-5Mn specimen - No.4; c - Fe-3Mn-0.9C specimen - No.13. Nital etched.](image)
The demanganisation of the specimens is documented by micrographs shown in Fig.9. Mainly the surface layers of the specimens in dependence on Mn and carbon content are due to demanganisation in various ranges ferritic. In terms of relative high interconnected porosity of the tested specimens, it is possible also to expect the demanganisation of the core grains.

The complex results of the mentioned measurements are listed in Tab.3. The shown minimum microconcentrations of manganese in margins and in cores of the specimens are lower than added manganese content, without some correlation to it at marked differences between the margin and the core. The margin, and of some steels the core areas of the specimens, were only ferritic.

Tab.3. Dimensional change ($\Delta l/l_0$), apparent hardness HV 10 (measured in the core), microanalysis of manganese concentration (Mn) (LINK analyzer) and the microhardness HV 0.02 (microhardness tester Hanemann) determined in the margin layer and in the cores of the cross-sections of the dilatometer specimens (Table 1). m – margin, c – core.

<table>
<thead>
<tr>
<th>Steel No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn added [%]</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Mn carrier</td>
<td>FeMn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron powder</td>
<td>SC 100.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*C_c graphite added [%]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta l/l_0$ [%]</td>
<td>-0.4</td>
<td>-0.4</td>
<td>-0.5</td>
<td>0.0</td>
<td>+0.4</td>
<td>0.0</td>
<td>+0.1</td>
</tr>
<tr>
<td>HV10 (centre)</td>
<td>100</td>
<td>107</td>
<td>112</td>
<td>177</td>
<td>95</td>
<td>117</td>
<td>151</td>
</tr>
<tr>
<td>Mn [%]</td>
<td>0.57- n. d.</td>
<td>0.37- n. d.</td>
<td>1.00- n. d.</td>
<td>1.17- 3.42</td>
<td>1.25- n. d.</td>
<td>0.13- 3.42</td>
<td>2.50-3.25</td>
</tr>
<tr>
<td>c</td>
<td>0.95- n. d.</td>
<td>1.81- n. d.</td>
<td>0.82- 3.51</td>
<td>0.62- 4.68</td>
<td>1.23- n. d.</td>
<td>1.06- 4.45</td>
<td>2.37-3.88</td>
</tr>
<tr>
<td>HV 0.02</td>
<td>118-202</td>
<td>174-333</td>
<td>133-362</td>
<td>117-166</td>
<td>122-206</td>
<td>115-191</td>
<td>134-309</td>
</tr>
<tr>
<td>c</td>
<td>137-386</td>
<td>146-426</td>
<td>131-386</td>
<td>108-306</td>
<td>126-222</td>
<td>116-176</td>
<td>136-282</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Steel No.</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn added [%]</td>
<td>2</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Mn carrier</td>
<td>FeMnC</td>
<td>FeMn</td>
<td>EMn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron powder</td>
<td>SC 100.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*C_c graphite added [%]</td>
<td>0.16</td>
<td>0.24</td>
<td>0.40</td>
<td>0.2</td>
<td>0.5</td>
<td>0.5</td>
<td>0.9</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta l/l_0$ [%]</td>
<td>+0.4</td>
<td>+0.3</td>
<td>+0.5</td>
<td>-0.1</td>
<td>+0.6</td>
<td>+0.3</td>
<td>+0.7</td>
<td>+0.5</td>
</tr>
<tr>
<td>HV10 (centre)</td>
<td>108</td>
<td>206</td>
<td>141</td>
<td>110</td>
<td>157</td>
<td>148</td>
<td>64</td>
<td>102</td>
</tr>
<tr>
<td>Mn [%]</td>
<td>1.68- n. d.</td>
<td>2.09-8.81</td>
<td>2.00-6.59</td>
<td>0.63-5.52</td>
<td>0.54-3.21</td>
<td>1.80- n. d.</td>
<td>0.77- n. d.</td>
<td>1.63- n. d.</td>
</tr>
<tr>
<td>c</td>
<td>1.77-5.94</td>
<td>0.52-5.12</td>
<td>1.01-5.57</td>
<td>2.75-3.62</td>
<td>1.62-4.20</td>
<td>2.05-4.53</td>
<td>0.95- n. d.</td>
<td>1.35- n. d.</td>
</tr>
<tr>
<td>HV 0.02</td>
<td>136-252</td>
<td>131-259</td>
<td>124-263</td>
<td>125-160</td>
<td>141-437</td>
<td>130-160</td>
<td>115-276</td>
<td>121-324</td>
</tr>
<tr>
<td>c</td>
<td>136-241</td>
<td>128-287</td>
<td>131-283</td>
<td>127-162</td>
<td>147-376</td>
<td>148-294</td>
<td>120-289</td>
<td>130-382</td>
</tr>
</tbody>
</table>

Remarks: *C_c - combined carbon added by FeMnC; $\Delta l/l_0$ of plain iron sample was +0.4%; each microhardness value is a mean value of 3 measurements; n.d - pearlite or bainite not observed optically.
The higher microconcentrations of manganese analyzed in the cores of the steels No.6, 8-12 proved the higher through alloying of some microareas by manganese in individual iron powder particles. This was affected by the heterogeneity of iron powder particles in austenite exhibited by higher structure and substructure diffusion activity for manganese. The relative higher microconcentrations of manganese in steels alloyed with FeMnC (steels No. 8-10) is to be noted as a consequence of the lower sublimation rate of manganese combined in cementite (Fe,Mn)\(_3\)C.

The minimum as well as maximum microhardness values are on the same level without relation to the manganese content added. This can be seen for instance for the steels No. 1-4 and 8-10.

The apparent hardness values are also on the same level without any effect of manganese content added in the range of 2 – 5%. (Low density of the tested dilatometer specimens must be considered).

Three-point bending tests were carried out on dilatometer specimens with a span 10 mm at loading rate ~1 mm/min for completing previous results. The results shown in Fig.10 do not represent an adequate relation to the manganese and carbon content. In bending tests there was not regarded the surface plane of the samples with which they were placed on the base of the dilatometer in relation to the effect of the loading force (the demanganisation of the dilatometer specimens in the test time was not documented anymore). This plane of the specimens was demanganised in a lower extent than other three surface planes. The results are only further proof of the demanganisation of the dilatometer specimens with the density of 6.6 g/cm\(^3\).

![Fig.10. Bending strength (T.R.S.) of the dilatometer Fe-Mn samples sintered for 60 min at 1150°C: left - in relation to the manganese content and iron powder grade; right - in relation to carbon content. Column: 1-5, 7, 8 - Mn added as FeMn, C added as graphite, 6 - C and Mn added as FeMnC.](image)

The presented results proved the demanganisation of the tested dilatometer specimens, which was necessarily demonstrated in lower final manganese content in the specimens. The dimensional changes of Mn containing steels determined by the dilatometry, Table 2, cannot be therefore accepted as objective characteristics.

The demanganisation of the dilatometer specimens is necessary to be evaluated separately in relation to their specific characteristics and to the proper sintering process. They differ in size, and in this case also in density from larger standard test bars and/or structural parts sintered in the boxes in laboratory and in industrial furnaces. The reverse sublimation of Mn from the dilatometer specimens into to atmosphere was improved by their large ratio surface/volume (272 mm\(^2\)/240 mm\(^3\)). This means they were exhibited by a large specific geometrical reaction surface area, e.g. 11.3 cm\(^2\)/cm\(^3\) compared, e.g. with the
impact strength bars (10 x 10 x 55 mm) with the geometrical reaction surface area of 4.4 cm$^2$/cm$^3$. Besides this, the total reaction surface area is markedly increased by the surface of the interconnected pores in the compact, which is much larger than the geometrical one. The specific surface area of an iron powder specimen with the density ~6.5 g/cm$^3$, as in this case, is about 150 mm$^2$/mm$^3$ [20]. The total reaction surface area of an individually processed dilatometer specimen would be about 360 cm$^2$, and the consequence of it was shown in large demanganisation of the specimens.

The shown large demanganisation observed in dilatometer specimens in terms of properties of sintered manganese steels is not acceptable. In reality, in the gas-phase alloying and sintering process of manganese steels, the “demanganisation” is a determining process, based on the physical property of manganese – high vapour pressure, which enables their sintering in the atmospheres of common industrial purity. The manganese escaping from the being sintered specimens – components in vapour form (Mn(g)) into the surrounding atmosphere, reacts there due to high affinity for oxygen with the oxygen in the flowing atmosphere to MnO. This process decreased the oxygen potential in the atmosphere to the equilibrium value given by the Mn/MnO line in the Ellingham-Richardson diagram as a result of the reduction – self-cleaning (protection) effect of manganese for sintering atmosphere [2,8-12].

The laboratory as well as industrial sintering of the Mn containing compacts occurs in batches of more pieces in one box. The sintered compacts are in such case mutually affected by manganese vapour, and by this the final manganese loss in individual compacts is minimized, up to negligible. The manganese loss is decreased also by markedly lower reaction surface area of the compacts with densities usually in the range of 6.8-7.1 g/cm$^3$ due to their lower specific geometrical and open pore surface area. The mechanical properties and corresponding microstructures of sintered manganese steels attained under different sintering conditions prove this statement, i.e. in [21-27]. In Figure 11 are shown the microstructures of hybrid Fe-Mo-Mn-C and of admixed Fe-Mn-C steels with the margins without demanganisation sintered under laboratory and industrial conditions, without special measures to eliminate possible oxidation of manganese carrier during sintering in an insufficiently clean atmosphere, or the demanganisation observed in the dilatometry test samples.
a - Fe-1.5Mo-2Mn-0.5C, Cc = 0.43%, Mn = 2.04%, 184 HV 10, ρ = 6.83 g/cm³

b - Fe-1.5Mo-4Mn-0.5C, Cc = 0.47%, Mn = 4.27%, 222 HV 10, ρ = 6.73 g/cm³

c - Fe-2.5Mn-0.8C, 195 HV 10, ρ = 6.88 g/cm³

d - Fe-3.0Mn-0.8C, 196 HV 10, ρ = 6.86 g/cm³

Fig.11. Microstructures of manganese containing steels showing margins of the specimens - components without demanganisation. a, b – hybrid Fe-1.5Mo-Mn-C steels, Ast.Mo, FeMnC, graphite, compaction at 600 MPa, laboratory sintering for 60 min at 1120°C, cracked ammonia, dew point -30°C [27]; c, d – Fe-Mn-C steels (component - roller of mass 125 g), SC100.26, FeMnC, graphite, compaction at 600 MPa, industrial sintering for 40 min at 1180°C, 70N₂/30H₂, inlet dew point -50°C [26]. Nital etched.

Enhancing effect of manganese for solid-state sintering

The linear shrinkage of the specimen’s length observed on the dilatometer graphs during the isothermal sintering was in previous chapters explained and analytically determined by demanganisation. The dimensional swelling at the beginning of the isothermal sintering, when it was in for all steels maximal, changed to “uniform” dimensional shrinkage with extending the holding time, as shown in Figs.1-7.

The sections of the dilatometer curves shown in Fig.12, enabled to particularize the view on the shrinkage of the Mn alloy steels compared to plain iron dimensional change. As can be seen in all sections, the shrinkage of the specimens with “lower” manganese content (Fe-(2,3)Mn and Fe-0.85Mo-(1,2)Mn) at the finish of the isothermal sintering was below the constant dimensional change of the iron compact. The traverse of this level was performed at a different time of the isothermal sintering.

This shrinkage, in the case for Fe-3Mn (Fig.1), and for Fe0.85Mo-1Mn (Fig.5) samples, was lower than for those containing carbon such as Fe-2Mn-0.16Cc (Fig.2a) and
Fe-3Mn-0.2C (Fig.2b) samples. This feature was a result of a further effect of the progressive effect of manganese not only on alloying, but as an enhancing effect of gaseous manganese for solid state sintering of manganese containing steels. As follows from all graphs, the shrinkage curves of the specimens in dependence on Mn content during the isothermal sintering were parallel. It means the effect of manganese as a sintering activator was constant and that the total shown shrinkage was the result of both, i.e. of the demanganisation and of the effect of the activated sintering caused by manganese. (There was no manganeseless sintered specimen, Table 2). The result of this feature was increased density of the being-sintered Mn containing steel specimens – components compared to the base without manganese addition. Besides this, higher shrinkage of Fe-Mn-C specimens (Figs.2a,b) compared to those without carbon (Figs.1,5) demonstrated the enhancing effect of manganese + carbon for sintering. Some data to this feature are as follow from Mn microanalysis listed in Table 2.

![Graphs](image)

CONCLUSIONS

The following results by the analysis of the dilatometer graphs of manganese containing steels were attained:

- The progressive linear swelling (expansion) of Fe-Mn-(C) steel samples and of those based on prealloyed Mo- and Cr- powders recorded by dilatometry proved the alloying of base powders by manganese in solid phase (base powder particle)-gas phase (Mn vapour) system in H₂/N₂ atmosphere with the dew point -30°C.

- The processing demonstrated increasing swelling of the specimens with increasing manganese addition during preheating up to the sintering temperature applied (highest values) compared to that of the iron specimen.
• The same dimensional changes for Mn containing steel samples at $\alpha$-$\gamma$ transformation temperature decreasing with increasing Mn content, had the same characteristic course as that of the iron sample.
• The beginning of the manganese sublimation was determined according to changes in the graphs was recorded to about 600°C.
• The various effects of sponge and water atomised iron powder was recorded in the values of the dimensional changes for the 2 and 3Mn samples. These were not observed in 5Mn samples. This reflects the state of through alloying of base austenite iron grains with manganese.
• The addition of carbon caused increased dimensional swelling in dependence on manganese as well as on carbon content. The different effect of combined carbon (added as FeMnC) as that of graphite was recorded. Carbon contributed to the retention of the differences in steels in dependence on Mn content, also during cooling.
• Various effects of manganese carriers on the swelling values of the Fe-Mn samples were recorded. This special attention needs the electrolytic manganese also in terms of maximal particle size – specific surface area used.
• The same character of dimensional swelling compared to the Fe-Mn-C steels was attained in testing the steels based on Mo and Cr prealloyed powders with addition of manganese and carbon forming the hybrid steels regarding some differences in dimensional changes of the base powder samples.
• Shrinkage of the dimensions of all tested steel samples during isothermal sintering was recorded compared to the highest values attained. This feature was caused by: a) demanganisation, and b) increased density of the samples as the enhancing effect of manganese for solid-state sintering. The observed large demanganisation was characteristic for the small-in-size and with high porosity dilatometer test samples used. This is not the case for laboratory as well industrially sintered common specimens - components.
• The recorded final dimensional changes do not characterize the individual Mn containing steels because of lower final manganese content due to demanganisation.

Acknowledgements

This work was supported by the Scientific Affairs Division within the framework of Science of Peace (NATO Project SfP 972395 'Development of Powder Metallurgy Manganese Steels for Structural Components') as solved by UOB Bradford, IMR SAS Košice and IMS BAS Sofia, 1999-2003 and by the Scientific Grant Agency of ME SR and SAS (Grant 2/6209/26).

REFERENCES

Metallurgy, vol. 48, 2005, no. 1, p. 23