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The Study of Local Effect of Manganese on Microstructure Development of Admixed Fe-Mn-C Sintered Steels

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Abstract: The present paper is focused on the effect of manganese on microstructure development of admixed Fe-Mn-C sintered steels along with diffusion characteristics of manganese in the iron matrix. Admixed systems were prepared on the base of sponge iron powder, with addition of 0.3% C and 3% Mn added as ferromanganese. Sintering at 1,023, 1,173, 1,323, 1,423 and 1,473 K for 180 s was carried out in laboratory tube furnace in an atmosphere of pure gases mixture 25% N₂ + 75% H₂ with the dew point of 243 K. The results show that admixed sintered manganese steels exhibit heterogeneity of microstructure due to the local chemical heterogeneities of these materials, in particular for those areas with a high manganese concentration. On the basis of calculation of manganese apparent diffusion coefficient and penetration depth, results reveal that diffusion-induced grain boundary migration (DIGM) is the dominant alloying mechanism in sintered manganese steels.

Keywords: sintered steels, microstructure, DIGM, diffusion coefficient

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Introduction

During the past decade huge expansion [1–11] in manganese sintered steels research is evident, where manganese additions have been tried in various forms, starting from elemental blended addition of various grades of ferromanganese and master-alloy powders up to fully pre-alloyed powder. However, its industrial utilization is still very

limited [12, 13] as sintering of admixed combinations leads to high risk of oxidation during heating stage and the high vapor pressure can result in significant loss of manganese even during the heating up phase [14–17]. This means that sintering condition during processing of admixed with Mn sintered steels required protective atmospheres of high purity due to the high affinity of Mn for oxygen which leads to the formation of continuous oxide network [18–20]. Utilization of fully prealloyed powders is restricted due to the expected lower compressibility of fully prealloyed powder owing to ferrite solid solution strengthening by Mn. Second drawback of manganese prealloyed powder is connected with some difficulties concerning decreasing of oxygen content to a reasonable level on industrial scale during production of water-atomized powders. However, modern industrial processes allow to reach reasonable quality of the manganese pre-alloyed powder that from the surface composition point of view is comparable with industrial Cr- or Mo-alloyed grades [21], which show definite advantages over admixed with manganese sintered steels [22].

Oxidation and/or reduction processes during the sintering are determined by reducing potential of used sintering atmosphere. For pure H₂ at any temperature, it is defined by the ratio of partial pressures of H₂ to H₂O. In the case of pure H₂ atmosphere it was shown [1, 16, 20] that there is a simple relationship between this ratio and water vapor content (dew point). It was established that the value of critical ratio at sintering temperature of 1,393 K is $p_{\text{H}_2\text{O}}/p_{\text{H}_2} = 5 \times 10^{-5} \text{ Pa}$ and $p_{\text{H}_2\text{O}}/p_{\text{H}_2} = 10^{-4} \text{ Pa}$ at sintering temperature of 1,523 K. If an atmosphere of pure H₂ is diluted with some inert gas, e.g. N₂ or Ar, its reducing potential is decreasing due to the reduction of available amount H₂ and so reduction of the partial pressures ratio of H₂ to H₂O. Wronski and Cias [20] postulated that the only effective way for a “good” sintering of admixed with Mn sintered steels is an active “micro-climate” around and within the compacts (manganese oxides are much harder to reduce even at high temperatures and low dew points). Therefore, authors [1, 16, 20] suggested that using of combinations of semi-closed container and getter can affect the thermodynamically governed reactions involving water vapor, iron, manganese and chromium oxides, carbon

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and hydrogen. Carbon in the compacts can produce CO_2 and CO due to carbothermal reduction of surface oxides and sintering conditions are controlled by the equilibrium ratio $p_{\text{CO}}/p_{\text{CO}_2}$ at a given temperature.

The aim of this work is to determine the effect of manganese on microstructure development of admixed Fe-Mn-C sintered steels along with the diffusion characteristics of Mn in the Fe matrix.

Material and experimental conditions

The raw materials used were commercial sponge iron powder SC 100.26 (Höganäs AB, Sweden), ferromanganese Elkem powder with particle size up to $40 \times 10^{-6} \text{ m}$ (Fe – 77.6% Mn – 1.4% C – 1.3% O), 0.3 wt% of natural graphite UF4 and commercial HW wax powder as lubricant. Two different powder mixtures were prepared – Fe-3Mn and Fe-3Mn-0.3C. Powder mixtures were homogenized in a Turbula mixer for 900 s. Cylindrical samples $\varnothing 13 \times 7 \text{ mm}^3$ were uniaxially pressed to the density of 7.0 g cm^{-3} without lubrication of the die wall. Sintering was carried out in a laboratory tube furnace in a nitrogen/hydrogen blend atmosphere (25% N_2 + 75% H_2) with the dew point of about 243 K. Specimens were sintered in semi-closed containers with a getter of Al_2O_3 + 10% FeMn + 5% graphite. The step sintering were carried out at 1,023, 1,173, 1,323, 1,423 and 1,473 K for 180 s. Heating rate was 10 K/s and cooling rate was 75 K/s. The sintering process is summarized in Table 1.

Following sintering, the specimens were cross-sectioned, metallographically prepared and examined by microstructure examination. Light and scanning electron microscopies were employed for microstructural evaluations. Following this specimens were cross-sectioned and polished to a surface finish of $1 \times 10^{-6} \text{ m}$ for examination in the scanning electron microscope (Tesla BS 340 with EDX LINK ISIS microanalyzer). The Mn content was measured using EDX-microanalyzer from the iron-ferromanganese particle interface. The thickness of boundary migration was determined by scanning microscopy inspections on at least 20 different zones, at high magnification and by using the linear

intercept method. The morphology change of ferromanganese particles during sintering processes was analyzed on polished surface of the ferromanganese (FeMn) specimens.

Results and discussion

Microstructure of FeMn particles in specimens Fe-3 Mn

The corresponding changes of FeMn particles after annealing at the temperatures of 750–1,200°C are presented in Figure 1(a)–(e).

Figure 1(a) shows specimens surface in the initial state after compaction where regularly shaped FeMn particle can be distinguished. Figure 1(b) shows the FeMn particles after sintering at 1,023 K indicating some changes in particle morphology even at this low temperature. These little changes of the FeMn particles surface are the consequence of the starting of manganese sublimation that increases considerably after ~1,013 K, causing an important redistribution of Mn in the vapor phase. This results in appearance of alloyed rims around FeMn particle even at such low temperature, see Figure 2 (a), (b).

This effect was firstly found and reported by Šalak [4, 23, 24] and represents an active alloying mechanism described before as diffusion-induced grain boundary migration (DIGM) [25]. This phenomenon of alloying with the presence of gas phase for iron-manganese system was firstly described by Navara [26] and further developed by other authors [27, 28]. DIGM is a recently recognized phenomenon that leads to unexpected motion of grain boundaries. Vastly enhanced mass transport characterizes the low-temperature aspect of the phenomenon, since the grain boundaries provide easy paths for diffusional redistribution of atoms in the regions traversed by the boundaries [29]. The measured values of mentioned thickness of alloyed regions at 1,173, 1,323 and 1,473 K are presented in Table 2.

The fine “sponge” morphology of the surface of FeMn particles occurs after the annealing at 1,173 K (Figure 1(c)). The annealing in the temperature in range of 1,323–1,473 K

Table 1: Materials and processing conditions.

Material	Temperature [K]	Atmosphere	Time [min]	Dew point [K]
Fe-3Mn	1,023–1,473	75% H_2 + 25% N_2	3	243
Fe-3Mn-0.3C	1,023–1,473	75% H_2 + 25% N_2	3	243

Figure 1: (a)–(f) Structure of FeMn particles in specimens Fe-3Mn; (a) as-pressed; (b) 750°C; (c) 900°C; (d) 1,050°C; (e) 1,150°C; (f) 1,200°C.

Figure 2: (a), (b) Microstructure of Fe-3Mn and Fe-3Mn-0.3C, respectively, after sintering at 750°C.

Table 2: The thickness of Mn-enriched area.

Material	$T = 1,173 \text{ K}$, thickness [10^{-6} m]	$T = 1,323 \text{ K}$, thickness [10^{-6} m]	$T = 1,473 \text{ K}$, thickness [10^{-6} m]
Fe-3Mn	4.76	7.22	17.85
Fe-3Mn-0.3C	5.46	7.81	18.05

results in the intensive changes of FeMn particles (Figure 1 (d)–(f)). During annealing at temperature of 1,473 K FeMn particle undergo significant changes in shape, size and surface morphology.

Microstructure developments

The microstructures of investigated materials are complex and heterogeneous, consisting of austenite, martensite, bainite and fine pearlite depending on the local Mn and C contents.

Microstructure of sintered at 1,173 K specimen, see Figure 3 (a), (b), consists mostly of the ferrite (original

Fe particles) and the pearlite regions close to the particles edges indicate start of the pearlite formation, see Figure 3(a).

Small pearlite islands are the result of carbon diffusion into the austenite. More extended Mn-enriched areas around FeMn particles indicate intensive manganese transport due to DIGM, see Figure 3(b). Intensive sublimation of manganese with temperature increasing promotes Mn redistribution in the vapor phase within the powder compact and increases Mn content on the prior powder surface of iron particles. The gradient of Mn concentration in iron matrix becomes a driving force for accelerated alloying which involved DIGM mechanism.

It should be noticed that investigated microstructures present the most alloyed regions around the pores in the places of the Mn sources. Manganese from the FeMn particles is concentrated around the pores and in the necks volume. It appears that the primary porosity inside iron powder is also relatively permeable. As the temperature increases, Mn vapor reacts with oxygen and water vapor. Formed oxides are accumulated in residual pores, in accordance with other authors [1, 6, 9, 11, 28]. Salak [15]

Figure 3: (a), (b) Microstructure of Fe-3Mn and Fe-3Mn-0.3C, respectively, after sintering at 900°C.

suggested that to utilize to the maximum extent the effect of sublimation and condensation of manganese vapors as a primary alloying mechanism, iron compacts must have mainly open pores, at least at the start of sintering, this ensures that by filling these pores the manganese vapors can affect the surface of all particles. Manganese vapor is supposed to be flowing, mainly through the secondary porosity. Ciaz et al. [7] postulated that manganese vaporized (sublimed) and was trapped in the pores. With the presence of oxygen and water vapor, even in the reduced dew point cases, it reacts with this vapor and/or resublimed into the pores seen in these measurements. The secondary porosity is originated from the sublimation of ferromanganese particles.

The ferromanganese donors, especially with high carbon content, are able to generate a liquid phase at sintering temperature of 1,393 K according to Castro et al. [28,30]. Due to the progressive diffusion of Fe atoms into the ferromanganese particles and of C atoms away from them and into the Fe matrix, lower stability of liquid phase in the case of low-carbon ferromanganese is expected. Analysis of this phenomenon was presented by Šalák [27]. A bulk diffusion equation for D_{Mn} in Fe_α and D_{Mn} in Fe_γ is presented by Nohara and Hirano [31, 32], as well Wells and Mehl [33] and Kučera and Stránský [34]:

$$D_{\text{MnFe}_\alpha} = 0.35 \cdot \exp \cdot \left(\frac{-219.8}{R \times T} \right) \quad (1)$$

and

$$D_{\text{MnFe}_\gamma} = 0.16 \cdot \exp \cdot \left(\frac{-261.7}{R \times T} \right) \quad (2)$$

where R [$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$] is the gas constant, and T [K] is the absolute temperature.

Calculations of diffusion coefficients and diffusion distances for Mn in Fe matrix after sintering at different temperatures with 180 s; along with experimental measured value are summarized in Table 3.

Table 3: Diffusion coefficients and diffusion distances for Mn in Fe matrix.

T [K]	t [s]	D [cm^2/s]	$x_{\text{calculated}}$ [10^{-6}m]	x_{measured} [10^{-6}m]
1,173	180	5.72×10^{-11}	0.29	4.76
1,323	180	7.46×10^{-12}	0.80	7.22
1,473	180	8.41×10^{-12}	1.24	17.85

It is clearly evident that the data of apparent diffusion coefficients in bulk manganese diffusion in Fe matrix are lower than data for sintered manganese steels. The highest values are registered due to mentioned characteristics of sintered system concerned with manganese evaporation, its condensation on iron powder particles surface and further transport by diffusion and diffusion-induced grain boundary migration mechanisms. The results shows that for investigated manganese sintered steels manganese travels into iron matrix up to 18×10^{-6} m in 180 s at the temperature of 1,473 K for both investigated systems. Amicarelli et al. [35] studied with the manganese diffusivity phenomena, compared sintered and wrought steels and determined that carbon migrates toward the manganese-rich zone due to the affinity of manganese for carbon. Manganese diffusion is enhanced by alloying elements. For equal times and temperatures the manganese diffusion depth of sintered steels is larger than in wrought steel of similar composition. Mitchell et al. [36] analyzed changes of manganese concentration in “three-layer” sintered specimens. Specimens were prepared on the basis of sponge iron powder NC 100.24 that formed border layers and medium layer was composed on the basis of ferromanganese. Specimens were sintered at temperature of 1,393, 1,423 and 1,453 K, respectively. The present results along with previous mentioned results [26–28, 35, 36] are in agreement with conclusions that DIGM is the dominant alloying mechanism in sintered manganese steels.

Manganese penetration depth

Mn penetration depth of scale analyses was calculated on the basis of microanalysis of Mn content along a distance from Mn source, represented by FeMn particles, using:

$$a = \frac{2 \cdot D^b \cdot \delta \cdot t}{l^2} \quad (3),$$

where D^b is the coefficient of grain boundary diffusion; δ is the width of the grain boundary; a is the Mn penetration depth.

Consequently, the penetration depth a was calculated according to eq. (3) using l from experiments and the coefficient of grain boundary diffusion, as [26]:

$$D^b = 6.35 \cdot 10^{-11} \text{m}^2 \cdot \text{s}^{-1},$$

and the width of the grain boundary:

$$\delta = 10^{-9} \text{m},$$

and the distance l from experiments at the time $t = 180 \text{ s}$ (Table 3).

Therefore, the results for sintering temperature of 1,173, 1,323 and 1,473 K in Fe-3Mn are listed in Table 4.

Table 4: The results of Mn penetration depth.

T [K]	$a_{\text{Fe-3Mn}}$ [10^{-6}m]	$a_{\text{Fe-3Mn-0.3C}}$ [10^{-6}m]
1,173	1.01	76.7
1,323	43.9	37.5
1,473	717	702

DIGM mechanism, along with intensive sublimation of manganese (occurring at high temperatures and promoting Mn redistribution in the vapor phase) and liquid phase presence at temperatures of 1,393 K, caused improved manganese distribution around the original Fe particle boundaries. Therefore, Mn distribution depths in the iron matrix are greater than those calculated for Mn volume diffusion.

Conclusions

Based on results of dependency of Mn contents in Fe matrix on the distance from manganese source (ferromanganese particles), the Mn penetration depth were calculated.

DIGM is the dominant alloying mechanism in sintered manganese steels.

Admixed sintered manganese steels exhibit heterogeneity of microstructure due to the local chemical heterogeneities of these materials, in particular for those areas with a high Mn concentration. The interpretation requires local approach on the base of chemical composition in particular point of interest. Presence of large contaminated pores from FeMn carrier particles (up to $20 \times 10^{-6} \text{ m}$) is another disadvantage in the case of the studied admixed steels.

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