Interfacial Reactions at Early Stages of Mn Addition to Liquid Fe

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Mn is an important alloying agent in steelmaking. Its interaction with liquid Fe during the alloying/deoxidation influences Mn recovery yield and steel cleanliness. We have experimentally studied the interfacial reactions at the early stages of Mn addition to liquid Fe containing various amounts of dissolved oxygen and sulphur. Diffusion couples were obtained by bringing liquid Fe into contact with solid Mn for various durations. After quenching these diffusion couples, the interdiffusion of Fe/Mn and the formation of a reaction zone at the Fe/Mn interface were investigated. The measured Mn concentration profile at the interface was fitted with a theoretical model based on Fick's second law. The magnitude of the fitted apparent diffusion coefficient suggested that a layer of Fe solidified around the cold Mn. While enclosed by this Fe shell, the Mn was partially molten due to its low melting temperature. The formation of oxysulphide inclusions was observed at the Mn-rich side of the interface, while an inclusion free zone was detected in the Fe-rich side close to the interface. Based on these experimental findings and theoretical calculations, the mechanisms governing the Fe/Mn interdiffusion and the inclusion free zone formation were proposed.

KEY WORDS: interfacial reaction; γ -FeMn; inclusions; diffusion couple.

1. Introduction

Manganese is an important alloying agent in steelmaking. Its addition to steel products improves their hardness and wear resistance.^{1,2)} Mn is also used as deoxidation and/or desulphurisation agent in steelmaking due to its strong affinity for oxygen and sulphur.³⁾ The deoxidation and/or desulphurisation products, *i.e.* Mn-containing inclusions (*e.g.* MnO and MnS) can be further utilized to minimize the harmful and maximize the beneficial effects of inclusions.^{4–6)} For instance, MnS can act as a lubricant between hard oxides and the steel matrix as a result of its low hardness and low melting temperature, thereby reducing their detrimental effects.^{4,5)} Moreover, Mn-containing inclusions (*e.g.* MnO–SiO₂–TiO_x–MnS type) are recognized as one of the most effective inclusions to act as nuclei for intragranular acicular ferrite (IGF),⁶⁾ which results in a reduced grain size and consequently improves the mechanical properties of these steel products. In particular, the Mn-depleted zone formed around Mn-containing inclusions can induce the IGF formation.

During ladle refining, pure Mn and/or FeMn alloy are added to the molten steel. To maximize the beneficial effect of Mn, its content has to be precisely controlled. Due to the high vapour pressure of Mn, its recovery yield can be significantly influenced by initial interactions with liquid Fe.⁷⁾ More importantly, the formation of oxide/sulphide inclusions at the early stages of Mn deoxidation (and/or alloying) determines the inclusion characteristics (such as inclusion size and size distribution, number density, morphology and

chemistry), and hence the steel properties.⁸⁾ To facilitate quantitative inclusion engineering, a deep understanding of their nucleation and growth, as well as thorough insight in the interdiffusion and interfacial reactions between Mn addition and a steel melt is required.

Interfacial reactions between alloying agents and molten steel have been investigated by several groups.^{9–13)} Argyropoulos *et al.* studied the dissolution of alloys (FeSi and Ti) by immersing them in molten steel.^{9,10)} They found that the dissolution consists of two stages, *viz.* the steel shell period and free dissolution period. During the former a layer of steel solidifies on the surface of the cold alloy. As the alloy is heated, this shell starts to melt. Free dissolution refers to the alloy dissolution in the liquid steel after the shell has melted. The initial stages of Al deoxidation were examined by Van Ende *et al.* with a liquid metal suction method.^{11,12)} They observed that the reaction zone was composed of successive layers of Fe–Al intermetallic compounds, as predicted by the Fe–Al phase diagram. Al₂O₃ inclusions formed in the Fe–Al reaction zone. It was demonstrated that the Al addition (around 5 g) melted completely before the shell (around 10 g) had molten. Pandelaers *et al.* focused on the interfacial reactions during Ti dissolution in molten steel,¹³⁾ showing that a liquid reaction zone is formed between the addition and the shell when their interface reaches the lowest eutectic temperature of the Fe–Ti system. Even though the melting point of Ti is higher than that of Fe, internal dissolution of Ti and Fe takes place, governed by coupled heat and mass transport. Pande *et al.* compared the dissolution behaviour of different Ti sources, *i.e.* Ti, FeTi35 and FeTi70 in liquid Fe. They found that FeTi35 was quickly dissolved due to its low melting temperature,

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and therefore less time was available for the modification of Al_2O_3 inclusions originally present in the FeTi alloy. FeTi70 was more easily dissolved than pure Ti, while its impurity elements like Al and Ca resulted in the formation of Al–Ti–O inclusions.¹⁴⁾ Literature on the Mn/liquid steel interfacial reactions, however, is limited. Specifically for the early stages of Mn deoxidation, knowledge is lacking concerning the microstructural development of the Mn/liquid steel interfacial region at high temperature, and concerning the reactions and inclusion formation at the Mn/liquid steel interface shortly after the deoxidation stage.

In this study the interactions between Fe and Mn shortly after the deoxidation stage were investigated by microstructural analysis of quenched diffusion couples, which are formed by bringing liquid Fe into contact with solid Mn for various durations. The interactions, *i.e.* Mn melting, inter-diffusion and the nature of the phases at the experimental temperature, were identified. These interactions depend on the thermal history, mass transfer and the supersaturation degree, which determine the nucleation and growth of the inclusions. The influence of the interaction time and the dissolved oxygen and sulphur content on the Fe/Mn inter-diffusion and formation of an inclusion free zone have been evaluated. Based on the experimental results and theoretical calculations, the mechanisms governing the Mn dissolution and the inclusion free zone formation were proposed.

2. Experimental

Fe_2O_3 and FeS (reagent grade) were mixed with 100 g electrolytic Fe (99.97% Fe) in a magnesia crucible. The crucible was then charged into a vertical tube furnace (GERO HTRV 100-250/18, MoSi_2 heating elements) and the mixture was melted at 1600°C under Ar atmosphere. The Ar was purified by passing over Mg chips at 550°C. The oxygen content in the off-gas was measured with a solid state ceramic oxygen sensor (Rapidox 2100), yielding a typical value of about 10^{-18} ppm. After the Fe was melted, the melt was stabilized at 1600°C for 60 min. A small piece of Mn (around 3 g in cubic shape, 99.8% Mn) was placed in a quartz tube. The end of the quartz tube was narrowed in order to maintain the Mn piece inside. The quartz tube with the Mn piece was then quickly introduced into the furnace and lowered into the melt (**Fig. 1(a)**). A small volume of liquid Fe was sucked and brought into contact with Mn for a designated interaction time (**Fig. 1(b)**). Thereafter, the tube was rapidly withdrawn from the furnace and quenched in water. The detailed conditions for each test are listed in **Table 1**.

The lower part of the obtained diffusion couple, which was Fe without Mn (**Fig. 2(a)**), was cut into small pieces (0.5–1.0 g) and cleaned with acetone in an ultrasonic bath. At least two pieces of Fe were analysed with LECO combustion analysis (TC-400 and CS-230) for total oxygen (T.O) and total sulphur (T.S) measurement. The measured values (average of two samples) are listed in Table 1. Since the impurity level of the electrolytic Fe was negligible, the measured T.O and T.S was considered to be, respectively, the dissolved [O] and [S] at experimental temperature. The upper part of the diffusion couple was mirror polished and subjected to microstructural characterization using electron

Fig. 1. Experimental set-up and procedure: (a) introducing the quartz tube into the melt and (b) bringing liquid Fe into contact with Mn.

Table 1. Experimental conditions, where T.O and T.S represent total oxygen and sulphur content in liquid Fe.

Test No.	Contact time (s)	Composition (ppm in weight)	
		T.O	T.S
1-a	2		
1-b	5	23	0
1-c	10		
2-a	2		
2-b	5	250	140
2-c	10		
3		489	444
4	5	955	0
5		34	505
6	10	1 657	3 570

probe microanalysis (FE-EPMA, JXA-8530F). Phases were identified using electron backscatter diffraction (EBSD, FEI XL30).

3. Results and Discussion

3.1. Overview of the Fe–Mn Diffusion Couple

The macroscopic examination of the Fe–Mn diffusion couple is shown in **Fig. 2(a)** (Test 6 as an example). After bringing liquid iron into contact with solid Mn for the pre-determined span, the cubic Mn piece has deformed into a cylindrical shape, suggesting that the Mn was melted in this short interaction time. Mn and Fe make good contact and macroscopically a reaction zone is observed (R-zone in **Fig. 2(a)**). **Figure 2(b)** shows a typical overview of the Fe–Mn diffusion couple (BSE image). Three phases, *viz.* α -Mn(Fe) (body-centred cubic, space group I43m), γ -FeMn (face-centred cubic, space group Fm3m) and α -Fe (body-centred cubic, space group Im3m)¹⁴⁾ are identified by using EPMA and EBSD analysis. Microstructurally, these various phases can be visually distinguished on the BSE image, as indicated by the dashed lines in **Fig. 2(b)**. Small cracks are found to be initiated from the α -Mn/ γ -FeMn interface, which may be due to the β -Mn/ α -Mn transformation. The β -Mn (simple cubic) is not stable at room temperature, and transforms

Fig. 2. (a) Macroscopic examination (test 6), where R-zone represents reaction zone and (b) BSE image of Fe–Mn reaction zone, and (c) Fe–Mn equilibrium phase diagram as calculated with FactSage.

Table 2. Mn content in Fe–Mn diffusion couple (wt%).

Phase	α -Mn(Fe)	γ -FeMn	α -Fe
Equilibrium at 25°C	81.4–100	–	0.4
Measured	70–99	40–70	–

upon cooling into α -Mn (body-centred cubic). The 5% cell contraction which accompanies this phase transformation may result in cracks.¹⁵⁾ The range of Mn content in the phases in Fig. 2(b) is measured with EPMA and listed in **Table 2**. The compositions of α -Fe and α -Mn(Fe) are in approximate agreement with those expected based on the Fe–Mn equilibrium phase diagram (Fig. 2(c)). The latter is calculated with FactSage, using the FSstel database. Referring to the phase diagram, γ -FeMn is not stable at room temperature (25°C) and would be expected to eutectoidally transform upon cooling into α -Mn(Fe) and α -Fe through Mn redistribution.¹⁶⁾ The presence of the pure γ -FeMn in the diffusion couple, however, is a result of the fast water quenching, which inhibits the Mn redistribution by limiting the Mn diffusion and freezes the ‘high temperature’ γ phase.¹⁷⁾

3.2. The Reaction Zone Development and the Diffusion Process

3.2.1. Fe–Mn Diffusion Couple without Oxygen and Sulphur Addition

During the experiment, a diffusion couple is formed between a solidified Fe shell and solid Mn (Fig. 2(b)). Inter-

diffusion of Fe and Mn results in the formation of a reaction zone, in which γ -FeMn is found between α -Fe and α -Mn(Fe) in the quenched sample. **Figure 3** shows the microstructural evolution of the reaction zone as a function of interaction time for Test 1 without extra oxygen and sulphur addition. The thickness of γ -FeMn is slightly larger after 5 seconds interaction (around 2 μ m in Fig. 3(b)) compared to 2 seconds (around 1 μ m in Fig. 3(a)), while it considerably increases and reaches 25 μ m after 10 seconds (Fig. 3(c)). The former indicates that only limited interdiffusion has occurred at the early stages of contact. This is because of (1) the limited time for Fe/Mn interdiffusion and (2) the formation of the solid Fe shell, *i.e.* the liquid Fe (1 600°C) solidifies on contacting the cold Mn (25°C).^{9–11)} This shell inhibits Mn diffusion in the liquid Fe. As can be seen in Fig. 3, an even γ -FeMn/ α -Fe interface (B-line, where no Mn is measured at the α -Fe side) observed in all samples implies a limited Mn diffusion into solid Fe (as can be seen in **Fig. 4**), while an irregular γ -FeMn/ α -Mn(Fe) interface suggests the presence of a liquid phase.¹⁸⁾ This is more obvious after 10 seconds interaction (Fig. 3(c)), where the thick, irregularly-shaped γ -FeMn layer is indicative for the presence of a liquid zone at the experimental temperature.

Figure 4 shows the measured Mn concentration for various interaction times as a function of the perpendicular distance from the diffusion front, *i.e.* the B-line in Fig. 3. The total diffusion distance and the thickness of these diffusion layers are measured and listed in **Table 3**. It should be noted that because the position of the initial Fe/Mn interface cannot be deduced from the quenched samples, the x-axis for the different curves lies not necessarily on the same absolute position. Distinct Mn concentration profiles can be observed in three layers, *i.e.* α -Mn(Fe), γ -FeMn and a thin layer (< 1 μ m) between γ -FeMn/ α -Fe (see bright line in Fig. 3). This thin layer is observed in all experimental samples, while its formation mechanism is not fully understood. Literature^{16,19,20)} reports that γ -FeMn containing 8–40 wt% Mn can be transformed into ε -FeMn (martensitic phase) during fast cooling. This, however, could not be verified in the present diffusion couple by using EBSD due to the uneven polished surface at the interface. In all samples, the Mn concentration gradient remains quite steep in the γ -FeMn layer. In the α -Mn(Fe) layer the gradient becomes flatter, although it changes considerably with diffusion time. After 10 seconds the reaction zone extends over about 2 000 μ m in α -Mn(Fe) compared to only around 300 μ m after 2 and 5 seconds (Fig. 4). The less steep concentration gradients in α -Mn(Fe) compared to those in γ -FeMn may be linked to the aggregation state (*i.e.* liquid or solid) at high temperature of different parts of the reaction zone.

To get a clear understanding of the state of the reaction zone during the experiment, the Fe/Mn apparent interdiffusion coefficient was estimated by fitting the measured Mn profile (in Fig. 4) with the theoretical model proposed by Fick’s second law

$$\frac{\partial C_{\text{Mn}}}{\partial t} = D \nabla^2 C_{\text{Mn}} \dots \dots \dots (1)$$

$$\frac{C'_{\text{Mn}} - C_{\text{Mn}}}{C'_{\text{Mn}} - C_{\text{Mn}}^0} = \text{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \dots \dots \dots (2)$$

Fig. 3. Interfacial microstructure with interaction time of (a) 2 s; (b) 5 s and (c) 10 s in Test 1 (23 ppm [O] in Fe), where B-line represents the bright line.

Fig. 4. Mn concentration profiles starting from the α -Fe/ γ -FeMn interface in Tests 1a, b and c measured with EPMA.

Table 3. The total diffusion distance (μm), the thickness (Thi in μm) and fitted apparent interdiffusion coefficient (D in m^2/s) of the sublayers in diffusion couple of Test 1.

	Mn content (wt%)	T1-a (2 s)		T1-b (5 s)		T1-c (10 s)	
		Thi	D	Thi	D	Thi	D
α -Mn(Fe)	70–100	280	4×10^{-9}	370	4×10^{-9}	2000	2×10^{-8}
γ -FeMn	40–70	1	4×10^{-14}	2	2×10^{-13}	25	1×10^{-11}
Total diffusion/ μm	–	~282		~373		~2026	

where C represents the Mn concentration, wt%; C' and C° respectively the Mn concentration at the phase boundary; t the time, s; and D the apparent interdiffusion coefficient, m^2/s , which can be obtained by solving the error function (Eq. (2)). During the calculation, following assumptions and

boundary condition are considered and used:

- (1). The interdiffusion is driven by the concentration gradient, and there is no convective contribution to mass transport in the tube.
- (2). The reaction zone is divided into three sublayers, *i.e.* the thin bright line, α -Mn(Fe) and γ -FeMn. To simplify the calculation, the interdiffusion in the sublayers is assumed to be independent.
- (3). For the γ -FeMn layer, $C_{Mn}^\circ = 40$ wt% and $C'_{Mn} = 70$ wt% at x_0 (interface between the bright line and the γ -FeMn layer) and x' (α -Mn(Fe)/ γ -FeMn interface), respectively.
- (4). For α -Mn(Fe) layer, $C_{Mn}^\circ = 70$ wt% and $C'_{Mn} = 100$ wt% at $x_0 = 0$ (α -Mn(Fe)/ γ -FeMn interface) and x' (α -Mn(Fe)/ α -Mn interface), respectively.

The thickness and fitted apparent interdiffusion coefficients of the sublayers are listed in Table 3. Due to the simplified assumptions as well as the scatter on the experimental points, only the order of magnitude is considered to be relevant. The results show that $D_{\alpha\text{-Mn}}$ is approximately 3 to 5 orders of magnitude larger than $D_{\gamma\text{-FeMn}}$. By comparing these data (Table 3) with literature,^{18,21–24} it is reasonable to conclude that the α -Mn(Fe) layer in Fig. 3 is the solidified Fe–Mn melt, which contains a small amount of Fe and is liquid at the experimental temperature; while the γ -FeMn layer consists of two contributions: (1) a thin solid γ -FeMn phase (at experimental temperature) close to pure Fe and (2) Fe–Mn melt, which transforms upon quenching into γ -FeMn. In addition, the apparent interdiffusion coefficient increases with holding time. This is more apparent in the γ -FeMn layer, where D has increased 3 orders of magnitude by increasing the holding time from 2 to 10 seconds (Table 3). This leap in the apparent interdiffusion coefficients implies that the γ -FeMn layer melts during the experiment due to the

continuous heat supply from the liquid Fe and the furnace. In the α -Mn(Fe) layer, the increase of the apparent interdiffusion coefficient with time is relatively limited, which confirms that this zone is already molten at an early stage.

Based on these considerations and observations with respect to the apparent interdiffusion coefficients and the microstructure of the reaction zone, the proposed development mechanism of the latter is schematically represented in Fig. 5: (a) there is a significant temperature difference between liquid Fe (1600°C) and solid Mn (around 25°C at $t=0$, Fig. 5(a)) before contact. It should be noted that although the Mn was quickly introduced into the furnace, it was preheated to some extent before contacting the liquid Fe; (b) a solid Fe shell forms at the initial contact interface with cold Mn (Fig. 5(b), $t=t_1$). Meanwhile the solid Mn partly melts due to its low melting temperature (1244°C); (c) the interdiffusion of Fe and Mn starts, *i.e.* Fe diffuses into liquid Mn and Mn into solid Fe (Fig. 5(c), $t=t_2$). As a result of the interdiffusion, γ -FeMn and liquid layers can form depending on the local Fe content and temperature (see phase diagram in Fig. 2(c)). With time, the solid Fe shell and the γ -FeMn layer partially melt due to the continuous heat supply from the melt and the furnace; (d) with a fast quenching, the liquid Fe–Mn melt transforms upon cooling into α -Mn(Fe) and γ -FeMn (Fig. 5(d), $t=t_3$)

depending on the local Fe content and cooling rate.

3.2.2. Fe–Mn Diffusion Couple with Oxygen and Sulphur Addition

The interfacial microstructure of samples of Test 2 with 250 ppm O and 140 ppm S addition to the steel is shown in Fig. 6. Compared to the diffusion without [O] and [S] addition, plenty of oxysulphide inclusions now form. The formation of Mn(O,S) inclusions is believed to be a consequence of the diffusion of Mn, O and S towards the diffusion front, where oxidation and sulphurisation reactions take place, Eqs. (3) and (4). In addition to the Mn(O,S) presence in γ -FeMn, two regions can be distinguished in the Fe-rich side (lower part of Fig. 6): one containing numerous Fe(O,S) inclusions and an “inclusion-free” region located between the bulk Fe and the Mn diffusion front. The former results from high [O] and [S] contents in liquid Fe, yielding Fe(O,S) upon solidification. The inclusion free zone suggests locally lower [O] and [S] contents at high temperature compared to the bulk Fe. The extent of Fe with low [O] and [S] contents determines the thickness of the inclusion-free zone. As most of the mass transport under the experimental conditions is assumed to be driven by diffusion, a thin inclusion-free zone corresponds to a steep [O] and [S] concentration profile near the diffusion front. As can be seen from

Fig. 5. Schematic evolution of the reaction zone.

Fig. 6. Interfacial microstructure with interaction time of (a) 2 s; (b) 5 s and (c) 10 s in Test 2 (250 ppm [O] and 140 ppm [S] in Fe).

Fig. 6, the thickness of this zone varies with holding time: after 2 s this zone is around 10 μm thick (Fig. 6(a)), whereas it reaches about 66 μm and 91 μm , after 5 s (Fig. 6(b)) and 10 s (Fig. 6(c)) respectively.

$$\Delta_{\text{M(O,S)}}^{\circ} = \frac{[\text{M}][\text{O}][\text{S}]}{[\text{M}]^{\text{eq}}[\text{O}]^{\text{eq}}[\text{S}]^{\text{eq}}} \quad \text{..... (5)}$$

where $\Delta_{\text{M(O,S)}}^{\circ}$ represents the local supersaturation of M(O,S), M = Fe or Mn; [M] and [M]^{eq} are respectively the local M and the equilibrated M concentration.

To help the understanding of the formation of the inclusion free region, **Fig. 7** shows a schematic of the reaction zone. The overlap between the Mn and [O] (and [S]) concentration profiles and the build-up of the supersaturation curve in the reaction zone at experimental temperature near the diffusion front is drawn. There are two reaction fronts, at which the Fe(O,S) and Mn(O,S) inclusions are found respectively. According to homogeneous nucleation theory, the supersaturation Δ° of inclusions (Eq. (5)) must reach a critical value Δ^* to initiate new nuclei.^{3,8,25} The reaction front appears when Δ° reaches Δ^* . Once nucleation occurs at the reaction front, supersaturation is rapidly consumed by inclusion formation, and the [O] and/or [S] decrease to their equilibrium contents at the reaction fronts. Immediately after contact, the liquid Fe is solidified and due to the high [O] and [S] contents in the Fe melt, Fe(O,S) inclusions are formed in the solidified Fe. On the other hand, the [O] and [S] react with Mn once the critical supersaturation of Mn(O,S) ($\Delta_{\text{Mn(O,S)}}^*$) is reached, forming Mn(O,S) inclusions at the Fe/Mn interface. The reaction results in a concentration gradient of [O] and [S], and consequently their diffusion from bulk Fe towards the reaction zone, leading to a decrease of [O] and [S] contents in the solidified Fe. At high temperature, the Fe(O,S) inclusions are not stable and tend to dissolved again in this [O] and [S] depleted (low) region once the supersaturation ($\Delta_{\text{Fe(O,S)}}^{\circ}$) is below 1. As shown in Fig. 7, an “inclusion free” region forms between the reaction front of dissolving Fe(O,S) and that of forming Mn(O,S). Due to the larger diffusivity of [O] and [S] in solidified Fe

Fig. 7. Schematic of the inclusion free zone formation, where solid [Mn], [S] and [O] lines represent their concentration; $\Delta_{\text{Fe(O,S)}}^{\circ}$ and $\Delta_{\text{Mn(O,S)}}^{\circ}$ respectively the local supersaturation of Fe(O,S) and Mn(O,S); $\Delta_{\text{Mn(O,S)}}^*$ the critical supersaturation for Mn(O,S) nucleation and $\Delta=1$ the equilibrium condition.

than that of Mn, the reaction front of Fe(O,S) dissolution moves faster than that of Mn(O,S) formation.^{26,27} With increasing interaction time, the diffusion of [O] and [S] from bulk Fe to the reaction zone proceeds, enlarging the area in the solid Fe with low [O] and [S] contents, and consequently resulting in a larger inclusion free zone. This agrees with the experimental observation in Fig. 6 that the thickness of the inclusion free zone increases over time.

Next to the inclusion free zone, γ -FeMn is also observed in qualitative similarity with the Fe–Mn diffusion couples without extra [O] and [S] additions (*i.e.* Test 1). Initially, *i.e.* after 2 seconds, a thin γ -FeMn zone is observed (Fig. 6(a) around 1 μm), which grows to 30 and 118 μm after 5 (Fig. 6(b)) and 10 seconds (Fig. 6(c)), respectively. The latter is much thicker than in Tests 1-b and 1-c (Figs. 3(b) and 3(c)), indicating that the reaction zone is significantly influenced by [O] and [S] addition.

3.3. Effect of Oxygen and Sulphur Contents

3.3.1. The Observed Interfacial Structure as a Function of Oxygen and Sulphur Content

Figures 8 (5 s interaction, Tests 1-b, 3, 4 and 5) and **9** (10 s interaction, Test 6) compare the interfacial microstructure for various [O] and [S] contents in liquid Fe. Similar with Tests 1 and 2, three phases, *i.e.* α -Mn(Fe), γ -FeMn and α -Fe are identified. By comparing Tests 1-b and 5, it is clear that for a constant holding time and [O] content (5 seconds and 23–34 ppm [O]), the thickness of γ -FeMn remains at a similar level (around 2 μm in Figs. 8(a) and 8(b)) even though the [S] content has increased from 0 to 505 ppm. This suggests that the [S] has limited influence on Fe/Mn stability regions of different phases. However, for a constant holding time and [S] (Figs. 8(a) and 8(c), *i.e.* Test 1-b vs Test 4, 5 s and 0 ppm [S]); Figs. 8(d) and 8(b), *i.e.* Test 3 vs Test 5, 5 s and 450–500 ppm [S]), the thickness of γ -FeMn differs strongly with varying [O] content. High [O] in the melt leads to a thick γ -FeMn zone and a rough or irregular γ -FeMn/ α -Mn(Fe) interface. With extremely high oxygen (1 660 ppm) and sulphur (3 900 ppm) addition (*i.e.* Test 6 in **Fig. 9**), a thick γ -FeMn layer (approximately 1 000 μm) was formed after quenching, and a large number of detached γ -FeMn fragments were found in the α -Mn(Fe) matrix. This confirms that high [O] leads to a large liquid reaction zone, resulting in fast Fe/Mn interdiffusion and a thick γ -FeMn layer upon solidification. On the other hand, Figs. 8 and 9 show that the thickness of the inclusion free zone decreases with increasing sum of [O] and [S] contents in the melt. In the following section, a fundamental analysis to understand the above observations (*i.e.* influences of oxygen and sulphur on the Fe/Mn interaction) will be given based on the measured Mn concentration profile and the calculated reaction heat exchange at the interface.

3.3.2. Influence on γ -FeMn Formation

Figure 10 summarizes the thickness of γ -FeMn (Fig. 10(a)) and the fitted apparent interdiffusion coefficients (Fig. 10(b)) as a function of [O] content in the melt. The thickness of γ -FeMn increases with [O] addition. This has been further corroborated by comparing the Mn profiles (at the Fe/Mn diffusion interface, **Fig. 11**) of samples with various [O] in liquid Fe. It is clear that the total diffusion length

Fig. 8. Interfacial microstructure for different oxygen and sulphur additions after 5 seconds interaction: (a) Test 1-b; (b) Test 5; (c) Test 4 and (d) Test 3.

Fig. 9. Interfacial microstructure of Test 6 with $[O] = 1\,600$ and $[S] = 3\,600$ ppm after 10 s holding.

(consisting of α -Mn(Fe) and γ -FeMn layers) changes with holding time, but not with oxygen content (see Fig. 11(b) around $2\,000\,\mu\text{m}$). The total diffusion length, here the pene-

Fig. 10. (a) γ -FeMn thickness and (b) fitted apparent interdiffusion coefficient as a function of $[O]$ content in the liquid Fe.

tration depth of Fe, roughly corresponds to the thickness of the liquid zone sandwiched between the solidified Fe and solid Mn. The liquid/solid interface at the Mn side is primarily determined by the melting rate of pure Mn, which is completely heat controlled. Since $[O]$ is the amount of dissolved oxygen in the Fe melt and it reacts with Mn only around the Mn diffusion front, *i.e.* solid Fe and γ -FeMn interface, it would not influence the melting rate of the pure Mn.

The increase in γ -FeMn thickness with $[O]$ should be

Fig. 11. Mn profile at the diffusion interface for various [O] contents in liquid Fe after (a) 5 s and (b) 10 s interaction.

related to its influence on the mass transport. Figure 11 shows a less steep Mn concentration profile with increase in [O], indicating enhanced Fe/Mn interdiffusion. By fitting the measured Mn concentration value with the theoretical model based on Fick's second law (Eqs. (1) and (2)), the apparent interdiffusion coefficient ($D_{\gamma\text{-Fe/Mn}}$) for different [O] levels was estimated and shown in the lower part of Fig. 10. Similar with the evolution of the $\gamma\text{-FeMn}$ thickness, the apparent interdiffusion coefficients strongly increase with oxygen addition. The leap of apparent diffusion coefficient is believed to be linked with the aggregation state (*i.e.* liquid or solid) of the diffusion zone with different [O] levels at high temperature.

To understand the influence of [O] and [S] on the reaction zone development, the liquid/solid ratio at the reaction zone was calculated (with the aid of FactSage, using databases FactPS, FSstel and FToxid) as functions of [O] and [S] contents. In the calculation, 1 g liquid Fe with various [O] and [S] contents (1 600°C) is equilibrated with 0.5 g Mn (25°C). The total enthalpy change is set to zero to obtain the adiabatic system temperature after reaction. The resulting liquid/solid ratio of the equilibrated products is shown in Fig. 12. This ratio rises substantially with increasing [O] and [S] contents in liquid Fe. The effect of [O] is much more pronounced than that of [S], which is in agreement with the experimental observations (Fig. 8). Based on the calculated results in Fig. 12, the liquid/solid ratio after reaction is expected to rise from 1 to 20% as the [O] changes from 0 to 1 660 ppm. This explains the leap in calculated apparent

Fig. 12. Influence of [O] and [S] content on liquid/solid ratio after reacting 1 g Fe (1 600°C) with 0.5 g Mn (25°C) as calculated with FactSage, index points can be used to read the predicted liquid/solid ratio at the experimental [O] and [S] contents.

Fig. 13. The evolution of inclusion free zone thickness as a function of the sum of [O]+[S] content in liquid Fe, where the dashed lines indicate the evolution tendency.

interdiffusion coefficients shown in the lower part of Fig. 10, *i.e.* $D_{\gamma\text{-FeMn}}$ increased 3 orders of magnitude by increasing [O] from 23 to 1 660 ppm. The contribution of [O] and [S] to the increase in the liquid/solid ratio is likely related to exothermic Mn oxidation/sulphurization reactions (Eqs. (3) and (4))^{25,27} at the Fe/Mn interface. In other words, the Mn oxidation and sulphurization reactions generate heat and raise the temperature at the initial Fe/Mn interface, forming more liquid phase. The later facilitates the Fe/Mn interdiffusion process, finally enhancing the $\gamma\text{-FeMn}$ formation upon quenching.

3.3.3. Influence on the Inclusion Free Zone Thickness

As seen in Fig. 13, the thickness of the inclusion-free zone generally decreases (not necessarily linear) with the sum of [O] and [S] content for a given interaction time. As discussed in section 3.2 (Fig. 7), the inclusion formation of Fe (O, S) and Mn(O,S) is believed to be a consequence of the diffusion of Mn, O and S towards the diffusion front, where oxidation and sulphurisation reactions take place. Therefore, transport and consumption of [O], [S], Mn and Fe determine the extent of inclusion-free zone formation. With high O and S contents, only a limited part of [O] and [S] can be consumed through the reactions with Mn at the

reaction front, and the remaining [O] and [S] are still high enough for Fe(O,S) inclusions to be present, leading to a narrow inclusion free zone. At extremely high [O] and [S] contents (1 600 ppm O and 3 900 ppm S), no inclusion free zone forms, as seen in Fig. 9. It should be noted that the heat release due to the oxidation and sulphurisation reactions will also influence the [O] and [S] diffusion in solidified Fe and consequently will affect the thickness of the inclusion free zone.

3.3. Comparison with Previous Studies

Van Ende *et al.* investigated the interfacial reactions between cold Al additions and liquid Fe by using a similar liquid metal suction method.^{11,12)} They did not establish the liquid or solid nature of the layers (FeAl and α -Fe(Al)) adjacent to the Fe shell. In the present paper, by fitting the apparent diffusion coefficient, the layer of γ -FeMn in the quenched diffusion couple is found to consist of a thin solid γ -FeMn and solidified Fe–Mn melt. In other words, this layer contains both liquid and solid fractions at experimental temperature. What's more, they reported that the inclusion free zone was in liquid state at experimental temperature.^{11,12)} According to the present observations and calculations (Figs. 5 and 7) however, the inclusion free zone is most likely formed in the solidified Fe shell. The calculation results show that the presence of oxygen in liquid Fe enhances the internal diffusion by locally raising the temperature at the initial Fe/Mn interface.

4. Conclusion

The interfacial reactions between cold Mn and liquid Fe containing various amounts of oxygen and sulphur were investigated with quenched Fe–Mn diffusion couples. The formation of alloy phases and their growth driven by interdiffusion was discussed. The influence of interaction time, dissolved oxygen and sulphur on the interdiffusion and formation of an inclusion free zone was quantitatively evaluated. The main results are summarized as follows:

(1) Three phases are identified in the quenched Fe–Mn diffusion couple, *i.e.* α -Mn(Fe), γ -FeMn and α -Fe. The thickness of α -Mn(Fe) and γ -FeMn increased with interaction time.

(2) The fitted $D_{\alpha\text{-Mn(Fe)}}$ in the quenched samples indicates that the α -Mn(Fe) layer is the solidified Fe–Mn melt, which contains a small amount of Fe and is liquid at the experimental temperature. The small $D_{\gamma\text{-FeMn}}$ and its significant increase during the experiment indicate that the γ -FeMn layer consists of two contributions: a thin γ -FeMn phase which is solid at experimental temperature and a Fe–Mn melt which transforms upon quenching into γ -FeMn.

(3) Based on these apparent interdiffusion coefficients

and the microstructure of the reaction zone, the latter's development mechanism is proposed. The liquid Fe solidified immediately after contacting the cold Mn. Meanwhile Mn melts due to its low melting temperature. Thereafter, Fe/Mn interdiffusion results in the formation of a FeMn interdiffusion layer. This reaction zone can be partially solid and liquid.

(4) Oxygen and sulphur additions locally raise the temperature by releasing chemical heat of oxidation and sulphurisation, consequently increasing the apparent interdiffusion coefficient of Fe/Mn at the α -Fe/ γ -FeMn interface, enhancing internal dissolution.

(5) An inclusion free zone is observed in the inner part of the Fe shell. With oxygen and sulphur addition, its thickness decreases, and it disappears for extremely high [O] and [S] contents ([O] > 1 600 and [S] > 3 600 ppm). Its formation is believed to be due to a local depletion of O and S, caused by the diffusion of Mn, S and O and oxidation/sulphurisation reactions at the diffusion front.

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