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Study on the Interfacial Reactions between an Fe–Mn–Si Alloy and Complex Oxides Containing FeO during Isothermal Heating

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Abstract: To precisely control the characteristics of complex oxides by heat treatment, the effect of FeO on the interfacial reactions that occur between an Fe–Mn–Si alloy and CaO–SiO₂–Al₂O₃–MgO–MnO–FeO oxide was studied and clarified. Eight types of diffusion couples with different compositions of oxides were produced using a confocal scanning laser microscope (CSLM). The morphologies of the alloy–oxide interfaces and the changes in their chemical compositions with isothermal heating at 1273 and 1473 K for 10 h were investigated. A modified dynamic calculation model was established and verified to achieve better understanding on the interfacial reaction mechanism between the Fe–Mn–Si alloy and the multicomponent oxide with different FeO content during isothermal heating. The results showed that during isothermal heating at 1273 and 1473 K, “solid–solid” and “solid–liquid” alloy–oxide reactions occurred in the A-1-*x* and A-2-*x* diffusion couples, respectively. The interfacial alloy–oxide reactions were enhanced by increasing the initial FeO content in the oxide and the heating temperature. The particle precipitation zone (PPZ), Mn-depleted zone (MDZ) and Si-depleted zone (SDZ) widths in the A-1-*x* and A-2-*x* diffusion couples after heating also showed a positive correlation with the increase in the initial FeO content in the oxide, as well as the size and number of MnO·SiO₂ inclusions. The diffused oxygen from the oxide reacting with elemental Mn and Si in the alloy plays a dominant role in the A-1-*x* diffusion couple during heating, whereas for A-2-*x*, the dominant reaction is between elemental Si in the alloy and MnO in the oxide.

Keywords: interfacial reaction; complex oxide; isothermal heating; FeO; Fe–Mn–Si alloy

1. Introduction

In general, to obtain super-clean steel products with high mechanical properties, such as fatigue resistance, tensile strength, and impact toughness, various compound deoxidizers with high efficiencies are used to reduce the dissolved oxygen and modify the non-metallic inclusions in molten steel [1,2]. MnO–SiO₂-type inclusions with low melting points and low hardness values are common modifications used to treat the inclusions in structural steel alloy during the refining process to avoid steel defects, such as stress cracks and fractures [3]. However, evidence indicates that the characteristics of the final inclusions in steel products after hot rolling and heat treatment are often different from those of the initial ones in molten steel. Shibata et al. [4] reported that the critical Si content in an Fe–Cr–Mn–Si steel in which the stable oxide changed from MnO–SiO₂ to MnO–Cr₂O₃ after heat treatment at 1473 K for 60 min was approximately 0.1 mass percent (pct) for 10 mass pct Cr steel and

0.05 mass pct for 5 mass pct Cr steel. Kim et al. [5] studied the reaction between a MnO–SiO₂–FeO oxide and an Fe–Mn–Si solid alloy during heat treatment using a diffusion couple method and proved the non-equilibrium state of the alloy and oxide during the heat treatment at 1473 K. Fine oxide particles and metal particles precipitated near the interface in the alloy and in the bulk oxide, respectively. Choi et al. [6] found that after heating at 1473 K, various inclusions from pure Al₂O₃ to TiO_x in three kinds of Fe–Al–Ti steels changed to Al–Fe–O, Fe–Ti–O, and Al–Ti–Fe–O inclusions, which also indicated that FeO content in the inclusions during heat treatment could be much higher than the equilibrium value in the molten steel at 1873 K. Liu et al. [7] introduced a new method for producing diffusion couples and studied the solid-state reaction between an Fe–Al–Ca alloy and Al₂O₃–CaO–FeO oxide at 1473 K. The widths of the particle precipitation zone and the aluminum-depleted zone in the alloy were shown to increase with the heat treatment time.

Previous studies have primarily focused on the modification of simple binary and ternary inclusions by heat treatment [8–10]. However, in practical steel production, most of the inclusions in Mn–Si deoxidized steels are complex CaO–SiO₂–Al₂O₃–MgO–MnO oxides, due to the interaction among the molten steel, refining slag and refractory material from the ladle lining [11]. In addition, because of the nonequilibrium among the molten steel, inclusions, and partial oxygen pressure in the system, FeO could also be present in the complex inclusions [6,12]. Therefore, to precisely control the characteristics of complex oxides by heat treatment, the effect of FeO on the “solid–solid” and “solid–liquid” interfacial reactions that occur between the Fe–Mn–Si alloy and the multicomponent oxide during heat treatment must be understood.

In this study, eight types of diffusion couples between an Fe–Mn–Si alloy and different complex oxides containing FeO were produced using a confocal scanning laser microscope (CSLM). The morphologies of the interfaces between the alloy and oxides and the changes in their chemical compositions after heat treatment at 1273 and 1473 K for 10 h were investigated. The mechanisms of the “solid–solid” and “solid–liquid” interfacial reactions and the element diffusion between the alloy and oxides were revealed and discussed from a thermodynamic perspective.

2. Experimental Methods

The initial compositions of the Fe–Mn–Si alloy and CaO–SiO₂–Al₂O₃–MgO–MnO–FeO oxides used to create the diffusion couples are shown in Table 1. The Fe–Mn–Si alloy was prepared by melting high-purity, electrolytic iron, manganese powder and silicon powder (Shanghai Macklin Biochemical Co., Ltd, Shanghai, China) in a vacuum induction furnace (Jinzhou Electric Co., Ltd, Jinzhou, China) with a 6.0 kg ingot. To create the CaO–SiO₂–Al₂O₃–MgO–MnO–FeO oxide, reagent grade CaO, SiO₂, Al₂O₃, MgO, MnO, and FeO powders (Shanghai Macklin Biochemical Co., Ltd, Shanghai, China) were fully mixed in a platinum crucible (Φ25 mm × 40 mm) and premelted in a high-temperature pipe furnace (Jinzhou Electric Co., Ltd, Jinzhou, China) under an Ar gas atmosphere. Then, the oxide was withdrawn from the furnace and rapidly cooled under an Ar stream. Thermogravimetry and differential thermal analysis (TG-DTA) (Beijing Hengjiu Experiment Instrument Co., Ltd, Beijing, China) was used to measure the melting points of the oxide variants, which were approximately 1358 K for oxide 1-0, 1-1, 1-2, and 1-3, and 1340 K for oxide 2-0, 2-1, 2-2, and 2-3. The concentrations of Mn, Si, and Fe in the alloys were analyzed using an electron probe microscopic analyzer (EPMA) (JEOL, Tokyo, Japan). The Ca, Si, Al, Mg, Mn, and Fe contents in the complex oxides were determined using inductively-coupled plasma-optical emission spectrometry (ICP-OES) (Thermo Fisher Scientific, Waltham, MA, USA) and were calculated based on the assumption that the oxides had stoichiometric components.

Table 1. Initial compositions of the Fe–Mn–Si alloy and CaO–SiO₂–Al₂O₃–MgO–MnO–FeO oxides used to create the diffusion couples.

No.	Fe–Mn–Si Alloy/Mass Percent (pct)			
	Mn	Si	Fe	S
A	0.60	1.31	98.09	0.0023

No.	CaO–SiO ₂ –Al ₂ O ₃ –MgO–MnO–FeO oxide/mass pct					
	CaO	SiO ₂	Al ₂ O ₃	MgO	MnO	FeO
1-0	27.10	43.00	13.70	5.80	10.40	0.00
1-1	26.83	42.57	13.56	5.74	10.30	1.00
1-2	26.29	41.71	13.29	5.63	10.09	3.00
1-3	25.75	40.85	13.02	5.51	9.88	5.00
2-0	26.70	39.30	12.90	5.40	15.70	0.00
2-1	26.43	38.91	12.77	5.35	15.54	1.00
2-2	25.90	38.12	12.51	5.24	15.23	3.00
2-3	25.37	37.34	12.26	5.13	14.92	5.00

To simulate the complex inclusions in the alloy and to investigate the interfacial reactions during the heat treatment, good contact between the Fe–Mn–Si alloy and the multicomponent oxide was necessary. The Fe–Mn–Si alloy was machined into a $\Phi 5.0 \text{ mm} \times 3.0 \text{ mm}$ cake, and a small circular hole ($\Phi 1.5 \text{ mm}$, depth: 2.0 mm) was created in the alloy to hold the oxide powder ($\sim 25 \text{ mg}$). The alloy and oxide were inserted into an Al₂O₃ crucible (O.D. 9 mm, I.D. 8 mm, height 3.5 mm) (Jidong Porcelain Factory, Tangshan, China) during the oxide premelting process in a confocal scanning laser microscope (CSLM) (Lasertec, Yokohama, Japan). When the overall pressure in the chamber reached $5.0 \times 10^{-3} \text{ Pa}$ after vacuum pumping (Partulab Technology Co., Ltd, Wuhan, China), Ar gas with a high purity (99.99 mass pct) was dried and then injected into the chamber to avoid oxidation of the specimens. The experimental temperature increased from room temperature to approximately 1700 K (40 K higher than the melting point of the oxide). As soon as the oxide melted, the power was shut off, and the specimen was immediately quenched in a helium stream. The heating and cooling rates were approximately 100 and 1000 K·min^{−1}, respectively. The experimental setup for the oxide premelting process is shown in Figure 1.

Figure 1. Experimental setup for the premelting of the oxide contained in the alloy cake by a confocal scanning laser microscope (CSLM).

To prevent the oxidation of the specimen during the heat treatment, each specimen, two bulk alloy blocks with the same composition and a piece of Ti foil, were sealed in a quartz tube after the oxide premelting process. The overall pressure in the tube was decreased to $1.0 \times 10^{-2} \text{ Pa}$ before

high-purity Ar gas was introduced into the tube to achieve a pressure of 2×10^4 Pa. The experimental setup for the vacuum sealing process is shown in Figure 2. Subsequently, the entire quartz tube was subjected to a heat treatment in a horizontal, high-temperature pipe furnace according to the designated temperature profile and then quenched with water. The entire temperature curve of the heating process including oxide pre-melting and the heat treatment process for the diffusion couples is shown in Figure 3. Here, “A” indicates the Fe–Mn–Si alloy. “1- x ” and “2- x ” indicate the two types of complex $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-MnO}$ oxides with different FeO contents, and “ x ” is equal to 0, 1, 2, or 3, which represent 0, 1, 3, or 5 mass pct FeO content in the oxide. The diffusion couple A-1- x was heated at 1273 K, whereas the diffusion couple A-2- x was heated at 1473 K. The isothermal heating time was 10 h. After the heat treatment, the specimens were fixed and embedded in a resin, and a longitudinal section of the diffusion couple was ground and polished by sandpaper and Al_2O_3 polishing paste ($0.3 \mu\text{m}$), respectively, and then coated with carbon powder for conduction. The morphology, chemical composition, and phases of the Fe–Mn–Si alloy and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-MnO-FeO}$ oxide for each alloy–oxide interface were observed, measured, and analyzed using EPMA. The elements in the alloy and oxide were calibrated using standard samples before every analysis to reduce the error.

Figure 2. Experimental setup for the vacuum sealing process.

Figure 3. Temperature curves for the isothermal heating of the diffusion couples.

3. Results

3.1. Effects of FeO on Solid–Solid Interfacial Reactions between the Alloy and Oxide after Isothermal Heating at 1273 K.

Figure 4 shows the morphologies of the interfaces between the Fe–Mn–Si alloy and the $\text{CaO–SiO}_2\text{–Al}_2\text{O}_3\text{–MgO–MnO–FeO}$ oxide in the A-1- x diffusion couples after isothermal heating at 1273 K for 10 h. Good contact between the alloy and the oxide was confirmed in all diffusion couples. As the FeO content in the oxide increased, particles and strip inclusions precipitated in the alloy near the interface. Their chemical compositions were similar to each other and close to $\text{MnO}\cdot\text{SiO}_2$, as determined using EPMA. White iron particles also appeared in the oxide for all diffusion couples after heating at 1273 K for 10 h except A-1-0. Generally, the size and number of these particles increased as the initial FeO content in the oxide increased. A positive correlation was observed between the width of the particle precipitation zone (PPZ), i.e., where the $\text{MnO}\cdot\text{SiO}_2$ inclusions form, and the initial FeO content in the oxide for the A-1- x diffusion couples. After isothermal heating at 1273 K for 10 h, as the FeO content increased from 0 to 1 to 3 to 5 mass pct, the width of PPZ increased from almost 0 to 2 to 5 to 8 μm , respectively. The experimental results suggest that “solid–solid” alloy–oxide reactions occurred during isothermal heating at 1273 K.

Figure 4. Morphologies of the interfaces between the Fe–Mn–Si alloy and $\text{CaO–SiO}_2\text{–Al}_2\text{O}_3\text{–MgO–MnO–FeO}$ oxide in the A-1- x diffusion couples after isothermal heating at 1273 K for 10 h: (a) A-1-0; (b) A-1-1; (c) A-1-2; (d) A-1-3.

Figure 5 shows the changes of Al, Ca, and Mg contents near the interface in the A-1- x diffusion couples after isothermal heating at 1273 K for 10 h. Slight diffusion from the oxide to the alloy is observed in Figure 5a,c for elemental Al and Mg, whose maximum contents in the alloy near the alloy–oxide interface in the A-1-0, A-1-1, A-1-2, and A-1-3 diffusion couples were all close to 0.02 mass pct. A significant increase of Ca content in the alloy near the interface was confirmed. After isothermal heating at 1273 K for 10 h, the maximum Ca content in the alloy in A-1-0, A-1-1, A-1-2, and A-1-3 diffusion couples was 0.386, 0.252, 0.219, and 0.353 mass pct, respectively. In the oxides of diffusion couple A-1- x , Al_2O_3 and CaO contents generally decreased toward the alloy–oxide interface. However, it is seen in Figure 5f that MgO content near the alloy–oxide interface increased from approximately 5.20 to 10.10, 10.26, 10.60, and 8.33 mass pct in A-1-0, A-1-1, A-1-2, and A-1-3 diffusion couples, respectively.

The changes in the Mn and Si contents in the alloy and oxide near the interface in the A-1- x diffusion couples after isothermal heating at 1273 K for 10 h are shown in Figure 6. Unlike the increasing Mn content trend at the alloy–oxide interface in the alloy of diffusion couple A-1-0, the Mn content of the alloy near the interface decreased from 0.60 to 0.472, 0.429, and 0.339 mass pct in diffusion couples A-1-1, A-1-2, and A-1-3, respectively, and the Si content also decreased from 1.31 to 0.232, 0.166, and 0.102 mass pct, respectively, as shown in Figure 6a,b. The results for diffusion couple A-1- x showed a negative correlation between the Mn and Si concentrations in the alloy near the alloy–oxide interface after isothermal heating and the initial FeO content in the oxide. In this study, the region with a lower Mn content than that of the bulk alloy is defined as the Mn-depleted zone (MDZ), and the region with a lower Si content is the Si-depleted zone (SDZ). According to experimental results

in diffusion couple A-1- x , as the initial FeO content increased from 0 to 1 to 3 to 5 mass pct, the width of MDZ increased from -15 to 25 to 27 to 29 μm , and the width of SDZ increased from 26 to 30 to 40 to 50 μm , respectively. The negative values for the MDZ width indicate the Mn content is higher near the alloy–oxide interface than in the bulk alloy. In Figure 6c,d, MnO in the oxide near the alloy–oxide interface decreased from approximately 10.0 to 5.67, 5.66, 5.50, and 3.06 mass pct, in A-1-0, A-1-1, A-1-2, and A-1-3 diffusion couples, respectively, whereas SiO_2 in the oxide near the interface increased from approximately 41.7 to 48.92, 47.66, 46.51, and 45.66 mass pct, respectively. Based on the experimental results, it was also confirmed that the decrease amplitude of MnO content and increase amplitude of SiO_2 content in the oxide after isothermal heating held positive and negative correlation with the initial FeO content in the oxide, respectively, which further suggested that “solid–solid” interfacial reactions occurred between the Fe–Mn–Si alloy and the CaO – SiO_2 – Al_2O_3 – MgO – MnO – FeO oxide.

Figure 5. Compositional changes of the alloy and oxide near the interface in the A-1- x diffusion couples after isothermal heating at 1273 K for 10 h: (a) Al; (b) Ca; (c) Mg; (d) Al_2O_3 ; (e) CaO ; (f) MgO .

Figure 6. Composition changes in the alloy and oxide near the interface in A-1- x diffusion couples after isothermal heating at 1273 K for 10 h: (a) Mn; (b) Si; (c) MnO; (d) SiO_2 .

3.2. Effects of FeO on Solid–Liquid Interfacial Reactions between the Alloy and Oxide after Isothermal Heating at 1473 K

Figure 7 shows the morphologies of the interfaces between the Fe–Mn–Si alloy and the $\text{CaO–SiO}_2\text{–Al}_2\text{O}_3\text{–MgO–MnO–FeO}$ oxide in the A-2- x diffusion couples after isothermal heating at 1473 K for 10 h. Good contact between the alloy and the oxide was also confirmed in all diffusion couples. “Solid–liquid” reactions occurred between the alloy and oxide. After the heating, when the initial FeO content was relatively high (3.0 and 5.0 mass pct in diffusion couples A-2-2 and A-2-3, respectively), many $\text{MnO}\cdot\text{SiO}_2$ inclusions precipitated in the PPZ of the alloy. The sizes of the $\text{MnO}\cdot\text{SiO}_2$ inclusions and PPZ widths were much larger than those in diffusion couples A-1- x after isothermal heating at 1273 K for 10 h, although this phenomenon was not obvious when the initial FeO content in the oxide was relatively low (1.0 mass pct in the diffusion couple A-2-1). Nearly no $\text{MnO}\cdot\text{SiO}_2$ inclusion was found in the alloy of diffusion couple A-2-0 near the interface after heating. Besides, larger iron particles were also observed in the oxide for all diffusion couples after heating at 1473 K for 10 h, except A-2-0. There was also a positive correlation between the width of PPZ and the initial FeO content in the oxide for the A-2- x diffusion couples. After the isothermal heating at 1473 K for 10 h, as the FeO content increased from 0 to 1 to 3 to 5 mass pct, the width of PPZ increased from 0 to 15 to 30 to 42 μm in diffusion couples A-2-1, A-2-2 and A-2-3, respectively.

Figure 7. Morphologies of the interfaces between the Fe–Mn–Si alloy and $\text{CaO–SiO}_2\text{–Al}_2\text{O}_3\text{–MgO–MnO–FeO}$ oxide in the A-2- x diffusion couples after isothermal heating at 1473 K for 10 h: (a) A-2-0; (b) A-2-1; (c) A-2-2; (d) A-2-3.

Figure 8 shows the changes of the Al, Ca, and Mg contents near the interface in A-2- x diffusion couples after isothermal heating at 1473 K for 10 h. The variation of Al, Ca, and Mg concentrations in the alloy of A-2- x diffusion couples were similar to those in the alloy of A-1- x diffusion couples. Slight diffusion of elemental Al and Mg from the oxide to the alloy and an obvious increase of Ca content in the alloy near the interface were also observed. After heating, the maximum Ca content in the alloy of diffusion couples A-2-0, A-2-1, A-2-2, and A-2-3 was 0.227, 0.235, 0.258, and 0.202 mass pct, respectively. In diffusion couple A-2- x , after isothermal heating at 1473 K for 10 h, the initial FeO content has a small influence on the changes of the Al_2O_3 , CaO, and MgO contents in the oxide. A slight decrease of CaO and MgO contents was observed with the increase of FeO content after the heating. Moreover, due to the rapid cooling rate, the oxide was relatively homogeneous in A-2- x diffusion couples.

The changes in the Mn and Si contents in the alloy and oxide near the interface in A-2- x diffusion couples after isothermal heating at 1473 K for 10 h are shown in Figure 9. After heating, the Mn content in the alloy increased from 0.60 to 1.75, 1.44, 1.31, and 1.15 mass pct, whereas the Si content decreased from 1.31 to 0.53, 0.29, 0.19, and 0.13 mass pct in the A-2-0, A-2-1, A-2-2, and A-2-3 diffusion couples, respectively, as shown in Figure 9a,b. Therefore, it was confirmed that with the increase in the initial FeO content in the oxide, the increase in amplitude of Mn content and the decrease in amplitude of Si content in the alloy near the interface decreased. After the heating at 1473 K, the overall MnO and SiO_2 contents in the oxide decreased and increased in A-2- x diffusion couples, respectively, without a region of gradual decline. In addition, FeO in the oxide further decreased the MnO content and increased the SiO_2 content of the oxide. As shown in Figure 9c,d, with the increase in the initial FeO content in the

oxide from 0 (A-2-0) to 1 (A-2-1) to 3 (A-2-2) to 5 mass pct (A-2-3), after the heating, MnO in the oxide decreased from 11.42 to 10.39 to 9.88 to 9.39 mass pct, whereas SiO₂ in the oxide increased from 41.28 to 41.44 to 41.93 to 42.38 mass pct, respectively.

Figure 8. Compositional changes of the alloy and oxide near the interface in A-2-*x* diffusion couples after isothermal heating at 1473 K for 10 h: (a) Al; (b) Ca; (c) Mg; (d) Al₂O₃; (e) CaO; (f) MgO.

Figure 9. Composition changes in the alloy and oxide near the interface in A-2-*x* diffusion couples after isothermal heating at 1473 K for 10 h: (a) Mn; (b) Si; (c) MnO; (d) SiO₂.

4. Discussion

4.1. Interfacial Reaction Mechanism between the Alloy and Oxide

In this study, the effect of the initial FeO content in the oxide on the “solid–solid” reactions at 1273 K and “solid–liquid” reactions at 1473 K between the Fe–Mn–Si alloy and the CaO–SiO₂–Al₂O₃–MgO–MnO–FeO oxide were investigated. Figure 10 shows the change in the FeO content of the oxide near the interface in A-1-*x* and A-2-*x* diffusion couples after isothermal heating for 10 h. In all cases, except A-1-0 and A-2-0 diffusion couples, the FeO content in the oxide decreased after heating. In A-1-1, A-1-2 and A-1-3 diffusion couples, the FeO decreased from 1, 3 and 5 mass pct to approximately 0.73, 1.11, and 1.83 mass pct, respectively. For the A-2-1, A-2-2, and A-2-3 diffusion couples, the “solid–liquid” reactions at 1473 K between the alloy and oxide further decreased the FeO content in the oxide from the levels attained in the “solid–solid” reactions at 1273 K to approximately 0.27, 0.30, and 0.44 mass pct, respectively. However, a slight increase in the FeO content in the oxide toward the alloy–oxide interface was observed. It is thought that Fe ions might have reacted with O ions of Al₂O₃, CaO, and MgO to form FeO_x, causing the diffusion of Al, Ca, and Mg from the oxide to the alloy during the heating. [13] Moreover, a previous study [14] has confirmed that during the secondary refining processes in steelmaking production, high-content calcium oxide in the refining slag decomposes into elemental Ca and O at the steel–slag interface. In this study, a similar decomposition reaction of CaO was expected to occur during isothermal heating at 1273 and 1473 K because the CaO content in the oxides were higher than 25 mass pct. Excess Ca diffused from the oxide to the alloy, which caused the increase in the Ca concentration in the alloy near the interface.

Figure 10. Change in the FeO content of the oxide near the interface in diffusion couples after isothermal heating at 1273 and 1473 K for 10 h: (a) A-1-*x*; (b) A-2-*x*.

According to the experimental results, FeO in the oxide decomposing into elemental Fe and O during isothermal heating was the primary cause of the decrease of FeO content. Excess O diffuses from the oxide to the alloy and reacts with elemental Mn and Si in the alloy in diffusion couples A-1-*x* and A-2-*x* to form MnO·SiO₂ particles. The reactions are shown in Equations (1) and (2). Diffusion of elemental Al, Ca, and Mg from the oxide to the alloy also occurred during heating, but this diffusion did not substantially influence the interfacial alloy–oxide reactions. A previous study also suggested that the elemental Si in the alloy could react with the MnO in the oxide during isothermal heating at 1273 and 1473 K, as shown in Equations (3)–(5) [15]. Thus, the two kinds of interface reactions together resulted in different experiment results in the diffusion couples A-1-*x* and A-2-*x*.

For the A-1- x diffusion couple, a “solid–solid” interfacial reaction occurred between the Fe–Mn–Si alloy and CaO–SiO₂–Al₂O₃–MgO–MnO–FeO oxide during isothermal heating at 1273 K. As the FeO content was 0 mass pct in the oxide of A-1-0, only Equation (5) occurred between the alloy and oxide near the interface, which caused the increase of Mn and SiO₂ contents and the decrease of Si and MnO contents. As the FeO content increased to 1, 3, and 5 mass pct in the oxide, Equation (2) became dominant to cause the decrease of Mn and Si contents, and the formation of MnO·SiO₂ inclusion in the alloy near the interface while the Equation (5) seemed to be secondary, which resulted in the decrease of MnO content and the increase of SiO₂ content in the oxide. However, as for the diffusion couple A-2- x during heating at 1473 K, a “solid–liquid” reaction occurred between the alloy and oxide. The dominant reaction varied to the displacement reaction between the Si in the alloy and the MnO in the oxide as shown in Equation (5), while Equation (2) turned out to be a secondary reaction. Therefore, generally, the Mn and Si contents of the alloy near the interface tended to increase and decrease, respectively, and the overall MnO and SiO₂ contents in the oxide decreased and increased, respectively, without a region of gradual decline. Among the diffusion couple A-2- x , as the initial FeO content in the oxide increased, the increase in amplitude of Mn content and decrease in amplitude of Si content in the alloy near the interface gradually decreased and increased, respectively, due to the secondary effect of Equation (2). An illustration of the interfacial reaction mechanism between the Fe–Mn–Si alloy and CaO–SiO₂–Al₂O₃–MgO–MnO–FeO oxide in diffusion couples A-1- x and A-2- x during isothermal heating is shown in Figure 11.

Figure 11. Illustration of the interfacial reaction mechanism between the Fe–Mn–Si alloy and CaO–SiO₂–Al₂O₃–MgO–MnO–FeO oxide during isothermal heating: (a) A-1-1, A-1-2 and A-1-3; (b) A-1-0 and A-2- x .

4.2. Dynamic Calculation Model

Although two kinds of interface reactions existed between the alloy and oxide in diffusion couples A-1- x and A-2- x during isothermal heating, the PPZ width was generally determined by the Equation (2). A dynamic calculation model based on Wagner theoretical equation which was used to calculate subscale layer thickness around surface cracks of steel products [16] has been modified and proposed to estimate the PPZ width in this study, as shown in Equations (6)–(8). The counter-diffusions of elemental Mn and Si in the Fe–Mn–Si alloy have also been taken into consideration [17].

$$\xi = [2N_{\text{O}} \cdot D_{\text{O}} \cdot F(z) \cdot t / (v \cdot N_{\text{B}})]^{1/2}, \quad (6)$$

where

$$F(z) = \pi^{1/2} \cdot \exp(z^2) \cdot \text{erfc}(z), \quad (7)$$

and

$$z = \xi / [2(D_{\text{B}} \cdot t)^{1/2}]. \quad (8)$$

In these equations, ξ represents the PPZ width in the alloy; D_{O} indicates the diffusivity of oxygen in the alloy which was obtained by Equation (9) for γ -iron at each temperature [18]; N_{O} represents

the mole fraction of oxygen at the alloy–oxide interface in which the value is determined by solubility of oxygen in the alloy; N_B and D_B represents the mole fraction and diffusion coefficient of the solute element in the alloy, respectively; ν indicates the number of oxygen atoms per A atom in AO_x oxide particle precipitated in the alloy; and t is reaction time. In this study, N_O was calculated by the FeO content in the oxide near the alloy–oxide interface during the isothermal heating. Therefore, according to our experimental results, N_O varied with the initial FeO content in the oxide after the heating for 10 h, as shown in Figure 10. The activity coefficient of FeO was obtained using Equation (10) [19]. N_O was determined by Equation (1). ν was obtained by assuming that only pure $MnO \cdot SiO_2$ particles were formed. N_B was calculated from the composition of the alloy used in this experiment, which was 0.0317. D_B was calculated according to the method proposed by Madelung [20].

$$\log D_O = -8820/T + 0.76, \quad (9)$$

$$RT \ln \gamma_i = \sum_j \alpha_{ij} X_j^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) X_j X_k + I'. \quad (10)$$

Figure 12 shows the experimental and calculated change of PPZ width with initial FeO content in the oxide of A-1- x and A-2- x diffusion couples after the isothermal heating for 10 h. Generally, after the isothermal heating, in the A-1- x diffusion couple, the observed PPZ widths show rough agreement with the calculated results by the dynamic model, while in the A-2- x diffusion couple, the calculated values are relatively higher than the experimental results. As the initial FeO content in the oxide increased from 0 mass pct to 1, 3, and 5 mass pct in the diffusion couple A-1- x , the interfacial reaction between the oxygen and elemental Mn and Si in the alloy for the formation of $MnO \cdot SiO_2$ inclusion plays a major role in determining the PPZ width. However, that interfacial reaction was weakened and affected by the displacement reaction between the Si in the alloy and the MnO in the oxide in the diffusion couple A-2- x during the heating, which resulted in the deviation between the calculated and experimental results. This dynamic calculation model is helpful to understand the interfacial reaction mechanism between the Fe–Mn–Si alloy and the $CaO-SiO_2-Al_2O_3-MgO-MnO-FeO$ oxide with different FeO content during isothermal heating.

Figure 12. Experimental and calculated change of PPZ width with initial FeO content in the oxide of A-1- x and A-2- x diffusion couples after the isothermal heating for 10 h.

5. Conclusions

The effect of FeO on the interfacial reactions that occur between an Fe–Mn–Si alloy and $CaO-SiO_2-Al_2O_3-MgO-MnO-FeO$ oxide was investigated using a diffusion couple method. The following conclusions were drawn:

- During isothermal heating at 1273 and 1473 K, “solid–solid” and “solid–liquid” alloy–oxide reactions occurred in A-1- x and A-2- x diffusion couples, respectively.

- With an increase in the initial FeO content in the oxide, the PPZ, MDZ, and SDZ widths increased in A-1-x and A-2-x diffusion couples after heating.
- Diffused oxygen from the oxide reacting with elemental Mn and Si in the alloy plays a dominant role in the A-1-x diffusion couple during heating, whereas in the case of A-2-x, the dominant reaction is elemental Si in the alloy reacting with MnO in the oxide.
- A modified dynamic calculation model was established and verified to achieve better understanding on the interfacial reaction mechanism between the Fe–Mn–Si alloy and the CaO–SiO₂–Al₂O₃–MgO–MnO–FeO oxide with different FeO content during isothermal heating.

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