Study of Mn absorption by complex oxide inclusions in Al-Ti-Mg killed steels

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Abstract

In Al-Ti-Mg killed steels, the use of complex deoxidation products, which act as heterogeneous nucleation sites for fine intragranular ferrite, has been acknowledged as an effective way for grain refinement. In this study, we investigated the interaction between Mn solute atoms and different oxide inclusions (such as MgO, MgTi₂O₄, MgTiO₃, Ti₂O₃, Ti₃O₅, Al₂O₃, MgAl₂O₄) experimentally and using first-principles calculations, to identify the oxides that can effectively lead to the formation of local Mn-depleted zones promoting the nucleation of intragranular ferrite. The results show that MgTi₂O₄, MgTiO₃ are effective for partition of Mn atoms into oxides, while MgO, Al₂O₃, MgAl₂O₄ are ineffective for the formation of local Mn-depleted zones. Furthermore, the calculations show that Mn atoms exist as a simple solute by

replacing Mg atoms in MgO, MgTi₂O₄ and MgTiO₃. Except by forming complex Ti-Mn oxides, such as MnTi₂O₄ and MnTiO₃, Mn atoms can also exist as a simple solute in Ti₂O₃ by occupying vacancy positions in their crystals. Ti₃O₅ oxides cannot absorb Mn atoms by replacing Ti atoms in it, meanwhile, the occupying vacancy pattern is not the main reason for Ti₃O₅ oxides absorb Mn atoms.

Keywords

oxides inclusions; Mn-depleted zones; ferrite; Al-Ti-Mg killed steels; DFT calculations

1. Introduction

In recent years, the alloy manufacturing [1], inclusion formation [2-5], grain structure evolution [6-9] and mechanical properties [10] of Al-Ti-Mg killed steels have been widely studied. Ti-Mg complex deoxidized steel can produce much dispersed composite inclusions, which enhance the formation of acicular ferrite. However, the effect of oxide inclusions in Al-Ti-Mg killed steels on the nucleation mechanism of intragranular acicular ferrite has been investigated seldomly so far.

Although a number of mechanisms have been proposed for the nucleation of acicular ferrite as non-metallic inclusions [11-23], the most widely accepted mechanism is that the Mn solute-depleted zone (MDZ) formed in the vicinity of an inclusion, can stimulate the formation of intragranular ferrite by increasing the chemical driving force for the austenite-ferrite transformation. In particular, among the many titanium oxides in Ti-bearing low carbon steels, Ti₂O₃, which effectively

absorbs a substantial amount of Mn resulting in a large MDZ, is believed to be the most effective nucleation site for the formation of intragranular ferrite [11, 14-22]. With regard to the origin of the local MDZ around Ti_2O_3 particles, there are two viewpoints: (i) the MDZ is produced by MnS precipitation on the Ti_2O_3 particles during the cooling process [18,20]; (ii) Ti_2O_3 itself can absorb Mn atoms from the steel matrix [11,23]. However, Shigesato et al. [22] demonstrated that a MDZ can also form without MnS precipitation on the Ti_2O_3 inclusion. Byun et al. [14] also showed the presence of a MDZ around individual Ti_2O_3 particles in wrought steels without MnS precipitation. Their observation could be explained by the fact that Ti_2O_3 has many cation vacancies, and that the radius of Mn ions is almost the same as that of Ti ions. However, there is no direct evidence, either by experiments or by calculations, showing that Mn ions can occupy vacancies or replace Ti ions in Ti_2O_3 . Therefore, knowledge on the absorption of Mn from the surrounding steel matrix by oxide inclusions in Al-Ti-Mg killed steels is of practical importance, since it will help us to understand the formation of MDZs around oxide inclusions and how their development can be maximized.

Commercial steels typically include a diversity of non-metallic inclusions that control the distribution of solute elements and affect the ferrite nucleation in various ways. This complexity limited the further development of experimental work to identify which non-metallic inclusions are effective in the formation of the MDZ. To guide further experimental work, first-principles calculation, based on density functional theory(DFT), can be used to rule out the interference of irrelevant

inclusions and impurities. This possibility attracted the attention of many researchers in the field of oxide metallurgy [12,17,24-26].

In this work, a combined experimental and theoretical method was developed to determine the inclusions that are effective in the formation of Mn solute depleted zones. First, SEM/EDS experiments were performed to demonstrate that, in Al-Ti-Mg killed alloys, in addition to the mechanism in which MnS precipitates on the inclusions, Mn can be absorbed by the inclusions themselves to form a MDZ, which induces the formation of intragranular acicular ferrite. Then, the interaction between Mn solute atoms and different oxide inclusions, namely MgO, MgTi₂O₄, MgTiO₃, Al₂O₃, MgAl₂O₄, was investigated by first-principles calculations to identify the oxides that are effective in the formation of local Mn-depleted zones. Finally, the characteristics of the Mn adsorption were analyzed using first-principles calculations for Ti₂O₃ and Ti₃O₅.

2. Experimental work

In previous work [9], the effect of aluminum on the inclusion characteristics and MnS precipitation behavior, as well as the effect of inclusions on the nucleation of ferrite in Al-Ti complex deoxidized magnesium treated steels, were systematically investigated. In this work, using the same experimental techniques, we show that, in addition to the formation through precipitation of MnS on inclusions, a MDZ, which induces the formation of intragranular acicular ferrite, can form by Mn absorption by the inclusions themselves. The experimental procedure and motivation for the choice of the steels are described in detail elsewhere[9]. The chemical composition is also

given **in supplementary information**.

The morphology and EDS mapping of the typical inclusions in as-cast S1 and S2 are shown in Fig.1. The oxides found in S1 were mainly Al-Ti-Mg-oxides and those in S2 Al-Mg-oxides. Fig.1(a), which is an illustration of a MgO inclusion core in the S1 alloy, shows that TiO_x precipitated on the surface of MgO, and MnS on the surface of TiO_x . Fig.1(b) shows co-precipitation of Al_2O_3 , MgO and TiO_x in the S1 alloy, and MnS on their surface. Fig.1(c), which illustrates the MgAl_2O_4 inclusion core found in the S2 alloy, shows a local precipitation of TiO_x and MnS on the surface of the MgAl_2O_4 inclusion. Fig. 1(d) shows the MgTiO_x and MgAl_2O_4 inclusion layers and the local precipitation of MnS on their surfaces. The Mn elemental distribution overlaps with the region of the MgTiO_x inclusion, while the Mn content is very low in the regions of MgAl_2O_4 , which indicates that MgTiO_x can absorb Mn atoms while MgAl_2O_4 cannot. Fig. 1(e) shows TiO_x inclusion layers and the Mn elemental distribution overlaps with the region of TiO_x inclusion.

It can be seen from Fig.1 that the Mg, Al, Ti and O atoms are distributed mainly in the center of the inclusion, the S atoms are mainly along the periphery of the inclusion and the Mn atoms are distributed both along the peripheries of all the inclusions and in the center of the TiO_x and MgTiO_x inclusions. Therefore, it can be inferred that MnS can precipitate on the surfaces of complex composite oxides, such as MgO, TiO_x , MgTiO_x or MgAl_2O_4 , and, in addition to MnS precipitation along the peripheries of complex inclusions, Mn can be absorbed by TiO_x and MgTiO_x , while MgO, Al_2O_3 , MgAl_2O_4 cannot absorb Mn atoms. The absorption of Mn by TiO_x and

MgTiO_x, inclusions during rapid cooling, leads to the formation of a narrow manganese-depleted zone (MDZ) near the inclusions.

It was reported that Ti₂O₃ oxide inclusions can promote nucleation of intragranular ferrite by the formation of a MDZ around Ti₂O₃ particles [11, 14-23]. To confirm that the MDZ, formed by absorption of Mn by MgTiO_x, induces nucleation of intragranular acicular ferrite, the transverse sections of S1 samples were examined with SEM/EDS. Fig. 2 shows a typical section of these samples. From this figure, it can be seen that Mn atoms are absorbed by MgO-TiO_x to form a MgO-TiO_x-MnO precipitate on one side of the Al₂O₃-MgO surface. A MDZ is formed in the vicinity of the MgO-TiO_x-MnO inclusion, with ferrite over it. Fig.2 illustrates that ferrite also forms on Al₂O₃-MgO. The EDS mapping of an Al₂O₃-MgO inclusion reveals that Mn atoms are not absorbed by Al₂O₃-MgO inclusions, suggesting that for these inclusions the formation of ferrite is through another mechanism than by the formation of a MDZ. Therefore, the formation of ferrite in the vicinity of Al₂O₃-MgO inclusion is not discussed in the present work.

3. Theory

3.1 Substitution and occupation balance calculations

Experimental results show that, in addition to MnS precipitation along the peripheries of complex inclusions, Mn can be absorbed by TiO_x and MgTiO_x, but not by MgO, Al₂O₃ and MgAl₂O₄. The interactions between Mn and MgO, Al₂O₃, and MgAl₂O₄ were first calculated using first-principles and compared with experiment

results to ensure the reliability of the calculation method. Then the absorption of Mn by MgTiO_x was investigated by first-principles calculation to further identify which oxide is effective in the local formation of MDZs.

The substitution and occupation models are deduced using partitioning enthalpy models of Ande [25]. Substitution enthalpies were first defined to describe the substituting Mn for cation positions in the oxides and in the *fcc* Fe matrix. The Mn substitution balance between *fcc* Fe and the oxide inclusions can be given as

where $Fe_{n-x}Mn_x$ and $A_{i-x}B_jMn_xO_k$ represent x Mn atoms dissolved in *fcc* Fe or in $A_iB_jO_k$ oxides.

This gives the substitution enthalpy as

$$H_s = (H[A_{i-x}B_jMn_xO_k] + H[Fe_n] - H[Fe_{n-x}Mn_x] - H[A_iB_jO_k])/x \quad (2)$$

where $H[A_{i-x}B_jMn_xO_k]$ is the total enthalpy at 0K. A positive H_s implies that Mn atoms partition to *fcc* Fe, and a negative H_s implies that Mn atoms are absorbed by the oxide inclusion.

It is well known that there are always some defects in the oxides, such as intrinsic defects (Schottky and Frenkel defects) and extrinsic defects. The occupation enthalpies for Mn occupying a vacancy in the oxide should thus be considered as well.

The Mn occupation balance for vacancy positions can be given as

where Fe_nMn_x and $A_iB_jMn_xO_k$ represent x Mn atoms dissolved in *fcc* Fe or in oxides,

This gives the occupation enthalpy as

$$Ho = (H[A_iB_jMn_xO_k] + H[Fe_n\Box_x] - H[Fe_nMn_x] - H[A_iB_jO_k\Box_x])/x \quad (4)$$

where $H[A_iB_jMn_xO_k]$ is the total enthalpy at 0K. A positive Ho implies that Mn atoms partition to *fcc* Fe, and a negative Ho implies that Mn atoms are absorbed by the oxide inclusion.

For the *fcc* Fe, in order to verify whether the paramagnetic(PM) phase can be reproduced by a nonmagnetic(NM) state, both NM and PM *fcc* Fe with Mn alloying element substitutions and occupations were considered. First, the NM *fcc* Fe was modeled with a 64 atom supercell, Fe_{64} , consisting of $2 \times 2 \times 4$ Fe unit cells with a total enthalpy of -511.203eV at 0 K. The dilute impurity solid solution was modeled by substituting one or two Mn atoms for Fe atoms and occupying one or two vacancies in the Fe cells with the (Mn) alloying element, giving the compositions $Fe_{63}Mn$, $Fe_{62}Mn_2$, $Fe_{64}Mn$ and $Fe_{64}Mn_2$, with a total enthalpy of, respectively, -512.861eV, -514.236329eV, -521.286eV and -529.006eV at 0K. Then, the PM *fcc* Fe with Mn impurities was modeled according to [27]. PM *fcc* Fe without Mn impurities was first modeled using the magnetic special quasirandom structure(SQS) technique. Alloys were considered as a collinear system with an equal amount of spin-up and spin-down atoms. The structural description of the 16-atom SQS structures with equal amounts of the two different kinds of atoms were listed in [28]. The total energy of SQS- Fe_{16} is -128.8931eV, obtained by the average of the energies of two magnetic configurations. The total energies at 0K of different magnetic distributions of Fe spins around Mn were calculated by changing the Mn positions inside the SQS used for the pure Fe. In our case, 16, 32, 16 and 16 positions of the impurity at different sites of the magnetic

SQS were used for $\text{Fe}_{14}\text{Mn}_2$, $\text{Fe}_{30}\text{Mn}_2$, Fe_{16}Mn and $\text{Fe}_{16}\text{Mn}_2$, respectively. The total energies of $\text{Fe}_{14}\text{Mn}_2$, $\text{Fe}_{30}\text{Mn}_2$, Fe_{16}Mn and $\text{Fe}_{16}\text{Mn}_2$ at 0K were obtained as -131.6356eV, -259.4381eV, -136.8115eV, and -137.4008eV by the average of the 16, 32, 16 and 16 groups of total energies, respectively. For $\text{Fe}_{15}\text{Mn}_1$, in order to ensure an equal amount of spin-up and spin-down atoms, $\text{Fe}_{30}\text{Mn}_2$ was considered in the calculations, and the energy of $\text{Fe}_{15}\text{Mn}_1$ was calculated approximately as the energy of $\text{Fe}_{30}\text{Mn}_2$ divided by 2. The structural description of the 32-atom SQS structures with equal amounts of the two different kinds of atoms were in the data of ATAT code and are listed in **supplementary information**.

At finite temperatures, substitution-free energy, rather than substitution enthalpy, should be used. However, it was demonstrated by Ande [25] that the two entropy contributions, one on either side of the balanced equation, largely cancel each other. It follows that, below 1000 K, the entropy contribution (TS) is about 0.1eV/atom at the most. Since the partitioning enthalpies are larger than 0.1eV/atom and the focus is on qualitative insights, it is possible to draw conclusions without considering the entropic contributions. Their first-principles density functional calculations at 0K could indeed qualitatively describe the partitioning of alloying elements between *bcc* Fe and cementite. In this work, the free energy of substitution of low-concentration-Mn for Mg in MgO inclusion at high temperatures was extrapolated using the Phonopy code to ascertain whether this “0K approximation” can be used in our calculations. For the PM state of *fcc* Fe, the impurity will sense many different magnetic configurations rather than only one. To catch the dynamic behavior of the magnetic system, different

Gibbs free energy for different configurations of paramagnetic Fe should be considered. Ponomareva[30] averaged the obtained energies for 50 different positions of the impurity at different sites of the magnetic SQS structures to give the potential energy of the paramagnetic alloy. For the considered structures in this study, with 16, 32, 16 or 16 positions of the impurity at different sites of the magnetic SQS, this approach would involve a large amount of computational work. Therefore, in this work, the Gibbs free energy of the PM SQS-Fe₃₀Mn₂ structure which has the smallest total energy at 0K of the 32 SQS structure groups was calculated using Phonopy code to ascertain the effect of temperature. The Gibbs free energy of SQS-Fe₁₅Mn₁ was half of the Gibbs energy of the SQS-Fe₃₀Mn₂ structure. The results show that despite the large difference in free energy of between the two conditions at 0K (-191.972eV for Mg₁₅MnO₁₆, -189.301eV for Mg₁₆O₁₆, -512.861eV for NM-Fe₆₃Mn, -511.203eV for Fe₆₄, -128.646eV for PM-Fe₁₅Mn, -129.992eV for PM-Fe₁₆) and 1000K (-199.700eV for Mg₁₅MnO₁₆, -196.867eV for Mg₁₆O₁₆, -543.739eV for NM-Fe₆₃Mn, -542.150eV for NM-Fe₆₄, -132.740eV for PM-Fe₁₅Mn, -134.288eV for PM-Fe₁₆), the calculated substitution enthalpies between those two conditions were 0.232eV/atom for NM-Fe and 0.362eV/atom for PM-Fe, which indicates that the entropy contributions on either side of the balanced Equations(1,3) largely cancel each other. Our calculated results in Section 4.1 show that all the substitution enthalpies are larger than 0.232eV/atom(NM) and 0.362eV/atom(PM) for MgO, and most substitution enthalpies are much more than that value, which indicates “0K approximation” are applicable in the deduced model for the prediction of Mn absorption by complex oxide inclusions. So the values

obtained from the first-principles calculations at 0K were used to save elaborate thermodynamic calculations.

3.2 Methodology

Calculation of this work have been performed using the Vienna ab initio simulation package(VASP) [29-31]under the framework of DFT [32]. A plane wave basis with a cut-off kinetic energy of 400 eV have been used throughout this work. The valence electron and core interactions were described, using the scheme of the Perdew-Burke-Ernzerhof(PBE) in generalized gradient approximation(GGA) [36]. During relaxation calculations, cell shape and volume are allowed to change. A conjugate-gradient algorithm is used to relax the ions into their instantaneous ground state. The Gaussian smearing method was used with a smearing width of 0.05eV. The relaxations were considered to be converged when all components of the residual forces are less than 0.01eV/Å. A final calculation was done without any relaxation using the Gaussian smearing method. The crystal structures obtained for all the compounds are listed in Table 1.

Table 1. The crystal structures of all the compounds

Oxides	Pearson symbol	Space group (No.)	Atom positions	Lattice parameters(Å)
MgTiO ₃ [34]	hR30	R-3(48)	O 0.34857,0.03943, 0.08815 Mg 0, 0, 0.1465 Ti 0,0, 0.35572	a = 5.0861, b = 5.0861, c = 14.0932, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$
MgTi ₂ O ₄ [35]	cF56	Fd-3m(227)	Mg 0, 0, 0 Ti 0.625,0.625,0.625 O 0.375, 0.375, 0.375	a = 8.474 , b = 8.474 , c = 8.474 , $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$
MgAl ₂ O ₄ [36]	cF56	Fd-3m(227)	Al 0, 0, 0	a = 8.155 , b = 8.155,

			Mg 0.375, 0.375, 0.375	$c = 8.155, \alpha = 90^\circ,$
			O 0.2378, 0.2378, 0.2378	$\beta = 90^\circ, \gamma = 90^\circ$
Al ₂ O ₃ [37]	hR30	R-3c(167)	Al 0, 0, 0.14783	$a = 4.7589, b = 4.7589,$
			O 0.30618, 0, 0.25	$c = 12.9919, \alpha = 90^\circ,$
				$\beta = 90^\circ, \gamma = 120^\circ$
MgO[38]	cF8	Fm-3m(225)	Mg 0, 0, 0	$a = 4.2198, b = 4.2198,$
			O 0.5, 0.5, 0.5	$c = 4.2198, \alpha = 90^\circ,$
				$\beta = 90^\circ, \gamma = 90^\circ$
Ti ₂ O ₃ [39]	hR30	R-3c(167)	O 0.30618, 0, 0.25	$a = 5.146, b = 5.146,$
			Ti 0, 0, 0.14783	$c = 13.541, \alpha = 90^\circ,$
				$\beta = 90^\circ, \gamma = 120^\circ$
Ti ₃ O ₅ [40]	mS32	C2/m(12)	Ti(m2a) 0.1276, 0, 0.5437	$a = 9.7568, b = 3.8008,$
			Ti(m2b) 0.0546, 0, 0.865	$c = 9.4389, \alpha = 90^\circ,$
			Ti(mi) 0.2219, 0, 0.2337	$\beta = 91.547^\circ, \gamma = 90^\circ$
			O(1) 0.233, 0, 0.746	
			O(2a) 0.051, 0, 0.344	
			O(2b) 0.13, 0, 0.06	
			O(3a) 0.328, 0, 0.439	
			O(3b) 0.408, 0, 0.153	

*m2a, m2b, mi, 1, 2a, 2b, 3a, 3b are the site notations of the atoms.

The five kinds of oxides (MgO, MgTi₂O₄, MgTiO₃, Al₂O₃, MgAl₂O₄) were modeled **using 1×1×1 (3×3×3 for MgO), 2×2×1 and 2×2×2 supercells**. A 2×2×1 k-point grid was used for integration over the 1×1×1 cells, **and a 1×1×1 k-point grid for these remaining cells**. The substitution was modeled by substituting one or two Mn atoms for the cation atoms and occupying one or two vacancy in the oxide supercells by Mn alloying element. Total energies of the NM-Fe structures with different positions of Mn impurity at different sites of the crystal structures were tested. It is found that the difference of the total energies of the NM-Fe structures with different Mn positions is less than 0.1 eV. To reduce the large computational work, we considered the Mn alloying element replacing cation atoms and occupying vacancies in NM *fcc* Fe and oxide supercells at random positions in their crystal structures.

Coordinates of the substitutions and occupation of Mn atoms in PM $\text{Fe}_{14}\text{Mn}_2$, F_{30}Mn_2 , F_{16}Mn_1 , $\text{Fe}_{16}\text{Mn}_2$ were listed in **supplementary information**. These 16, 32, 16, 16 groups of the $\text{Fe}_{14}\text{Mn}_2$, F_{30}Mn_2 , F_{16}Mn_1 , $\text{Fe}_{16}\text{Mn}_2$ magnetic SQS structure were obtained by the exchange of “spin up” and “spin down” for Fe atoms in the magnetic SQS structure.

4. Calculation results and discussion

4.1 The interaction of Mn with MgO , MgTi_2O_4 , MgTiO_3 , Al_2O_3 and MgAl_2O_4

Table 2 and Fig. 3 are the substitution enthalpies for oxides in which Mn atoms are substituted for Mg, Ti or Al atoms. Both NM and PM configurations of *fcc* Fe were considered. It can be seen that the substitution enthalpies of Mn are negative for MgO , which indicates that Mn atoms from the steel matrix can be absorbed by MgO . However, the experimental result from Fig. 1 shows that MgO cannot absorb Mn, while Mg and Ti can form stable complex oxides. From the calculated substitution enthalpies, in combination with the experimental result, one can conclude that MgO is more likely to absorb Ti, rather than Mn, when Ti is present in the melt. The substitution enthalpies are positive for Al_2O_3 ; so, Mn atoms from the matrix cannot be absorbed by Al_2O_3 . **Except for two near-zero negative values in NM Fe state and three near-zero negative values in PM Fe state, the substitution enthalpies are positive for replacement of Mg and Al atoms by Mn atoms in MgAl_2O_4 ; therefore, MgAl_2O_4 has very weak ability to absorb Mn atoms. And, these results can also**

suggest that substitution of only one atom in one kind of supercell cannot give a comprehensive solution that reflects the objective reality. The calculation results are consistent with the experimental results, indicating that the deduced models give reliable predictions of the interaction of Mn with MgO, Al₂O₃ and MgAl₂O₄ inclusions.

The substitution enthalpies are positive for Ti replaced and negative for Mg replaced by Mn in MgTi₂O₄ and MgTiO₃, which indicates that, when Mn atoms diffuse into the oxides, MgTi₂O₄ and MgTiO₃, they will be absorbed by replacing Mg atoms in the crystal structure. It can also be seen from Table 2 and Fig. 3, decreasing the supercell size and increasing the number of absorbed Mn atoms (both increasing the Mn concentration) change the substitution enthalpy in the same direction, namely, with increasing Mn concentration, the substitution enthalpies for Mg replacement decrease for MgTiO₃, and increase for MgTi₂O₄.

The occupation enthalpies obtained for the five oxides, in which vacancies are occupied by Mn atoms, are shown in Table 3 and Fig. 4. From these results, it can be seen that the occupation enthalpies are positive for all five oxides when Fe in its NM state, but there are one and two near-zero negative value for MgTi₂O₄ and MgTiO₃ respectively when Fe in its PM state. That indicate Mn atoms absorbed to these oxides by occupying vacancies in the crystal was not the main reason to form MDZ.

Table 2 Substitution enthalpies for five oxide supercells in which Mn atoms are substituted for Mg, Ti or Al atoms

Substitution situation	Hs[eV/Mn atom]				
	MgO	MgTi ₂ O ₄	MgTiO ₃	Al ₂ O ₃	MgAl ₂ O ₄
1Mn(Mg) 3×3×3 MgO, 1×1×1 others (NM)	-0.976	-2.069	-1.430	-----	0.617
1Mn(Mg) 3×3×3 MgO, 1×1×1 others (PM)	-1.808	-2.901	-2.262	-----	-0.215
2Mn(Mg) 3×3×3 MgO, 1×1×1 others (NM)	-1.269	-0.717	-1.640	-----	0.404
2Mn(Mg) 3×3×3 MgO, 1×1×1 others (PM)	-1.414	-1.891	-1.786	-----	0.259
1Mn(Mg) 2×2×1 (NM)	-0.357	-2.870	-1.389	-----	-0.197
1Mn(Mg) 2×2×1 (PM)	-1.189	-3.702	-2.221	-----	-0.409
2Mn(Mg) 2×2×1 (NM)	-1.715	-2.217	-1.600	-----	-0.476
2Mn(Mg) 2×2×1 (PM)	-1.860	-2.362	-1.745	-----	0.199
1Mn(Mg) 2×2×2 (NM)	-0.964	-5.979	-1.371	-----	0.563
1Mn(Mg) 2×2×2 (PM)	-1.796	-6.811	-2.203	-----	-0.269
2Mn(Mg) 2×2×2 (NM)	-1.306	-3.307	-1.332	-----	0.563
2Mn(Mg) 2×2×2 (PM)	-1.452	-3.452	-1.477	-----	0.418
2Mn(Ti or Al) 1×1×1 (PM)	-----	3.272	5.813	1.224	1.045
1Mn(Ti or Al) 2×2×1 (NM)	-----	4.382	5.506	1.623	1.544
1Mn(Ti or Al) 2×2×1 (PM)	-----	3.5450	4.674	0.791	0.712
2Mn(Ti or Al) 2×2×1 (NM)	-----	2.878	5.524	1.092	1.274
2Mn(Ti or Al) 2×2×1 (PM)	-----	2.733	5.3782	0.947	1.371
1Mn(Ti or Al)2×2×2 (NM)	-----	1.496	6.539	1.646	1.681

1Mn(Ti or Al) 2×2×2 (PM)	-----	0.664	5.707	0.814	0.849
2Mn(Ti or Al) 2×2×2 (NM)	-----	1.733	5.698	1.389	1.293
2Mn(Ti or Al) 2×2×2 (PM)	-----	1.588	5.552	1.243	1.148

Table 3 Occupation enthalpies for five oxide supercells in which the vacancies are occupied by Mn atoms

Occupation situation	Ho[eV/Mn atom]				
	MgO	MgTi ₂ O ₄	MgTiO ₃	Al ₂ O ₃	MgAl ₂ O ₄
1Mn 3×3×3 MgO, 1×1×1 others (NM)	12.632	7.864	17.723	21.168	11.298
1Mn 3×3×3 MgO, 1×1×1 others (PM)	10.468	5.699	15.558	19.003	9.133
2Mn 3×3×3 MgO, 1×1×1 others (NM)	11.380	6.732	4.047	7.154	8.386
2Mn 3×3×3 MgO, 1×1×1 others (PM)	6.732	2.084	-0.601	2.506	3.738
1Mn 2×2×1 (NM)	12.667	7.318	3.681	9.563	10.924
1Mn 2×2×1 (PM)	10.502	5.153	1.517	7.398	8.759
2Mn 2×2×1 (NM)	11.327	4.041	4.345	12.975	9.468
2Mn 2×2×1 (PM)	6.680	-0.607	-0.303	8.327	4.821
1Mn 2×2×2 (NM)	12.204	3.197	13.086	4.961	8.850
1Mn 2×2×2 (PM)	10.039	1.033	10.921	2.796	11.014
2Mn 2×2×2 (NM)	13.155	4.647	7.361	12.525	9.548
2Mn 2×2×2 (PM)	6.144	0.049	2.714	7.877	4.900

4.2 The interaction of Mn with Ti₂O₃ and Ti₃O₅

Although the absorption of Mn into the Ti_2O_3 layer has been experimentally demonstrated [11,23], it has not been elucidated whether Mn is present as a simple solute in the Ti_2O_3 oxide or whether a complex Mn-Ti-O oxide is formed. Two mechanisms are considered to be possible. (i) Mn atoms occupy vacancies or replace Ti atoms in the Ti_2O_3 structure [11,23]. Shim [23] inferred that the Mn ions from the steel matrix are absorbed into vacancies of Ti ions of Ti_2O_3 particles, since the structure of Ti_2O_3 has a significant number of vacancies, and the radius of Mn ions is very similar to that of Ti ions in Ti_2O_3 . (ii) Ti_2O_3 oxides absorb Mn atoms by forming complex oxides. Byun et al. [14] investigated the phase composition of non-metallic inclusions in Ti-deoxidized C-Mn steels and found Mn_2TiO_4 and MnTiO_3 oxides in steel T20.

Substitution enthalpies for Mn atoms replacing Ti atoms or occupying vacancies in the Ti_2O_3 and Ti_3O_5 structure were calculated, and the results are shown in Table 4 and Fig.5. It can be seen that the properties of the paramagnetic (PM) austenite phase are not well reproduced assuming a nonmagnetic(NM) state in the calculations. The enthalpies are positive for substitution and vacancy occupation for Ti_2O_3 when *fcc* Fe is in the NM state; thus, different from the hypothesis of [14,26], our calculations show that Mn atoms can neither replace Ti atoms nor occupy vacancies when Mn atoms diffuse into the Ti_2O_3 oxides. But when *fcc* Fe was calculated in the PM state, although the enthalpies are positive for substitution, three enthalpies for vacancy occupation are negative. That is consistent with the hypothesis of [14,26]. Considering Byun's experimental results, it can be concluded that the absorption of

Mn from the steel matrix into the Ti_2O_3 particles dispersed in the steel can occur both by a change in crystal structure forming a new stable Mn-Ti complex oxide and by occupying vacancy positions in Ti_2O_3 crystal.

The enthalpies are positive for substitution and vacancy occupation for Ti_3O_5 when *fcc* Fe is in the NM state, but there are two near-zero negative enthalpies for vacancy occupation. That means that Ti_3O_5 oxides cannot absorb Mn atoms through the replacement of Ti atoms by Mn atoms and that absorption of Mn atoms by occupying vacancy positions cannot be an important mechanism. Kang[41] performed a series of thermodynamic analyses to elucidate possible mechanism of MDZ development near Ti oxide inclusions. The Ti_3O_5 inclusion in their calculation is found to transformed into Mn-Ti complex oxides or Ti_2O_3 . Considering Kang's[37] calculation results, it is reasonable to believe that the absorption of Mn from the steel matrix into Ti_3O_5 particles can occur both by a change of the original crystal structure to form new stable Mn-Ti complex oxides or by a change of the structure to Ti_2O_3 oxides that absorb Mn.

Table 4 Substitution and occupation enthalpies for Ti-oxides in which Ti atom positions or vacancies occupied by Mn atoms

Substitution situation	Hs[eV/Mn atom]				Ho[eV/Mn atom]	
	Ti_2O_3	$\text{Ti}_3\text{O}_5(\text{m2a})$	$\text{Ti}_3\text{O}_5(\text{m2b})$	$\text{Ti}_3\text{O}_5(\text{mi})$	Ti_2O_3	Ti_3O_5
1Mn 1×1×1 (NM)	4.035	3.706	4.443	4.439	4.563	8.553
1Mn 1×1×1 (PM)	3.202	2.873	3.611	3.607	2.399	6.388

2Mn 1×1×1 (NM)	3.811	3.707	4.221	4.212	3.311	4.368
2Mn 1×1×1 (PM)	3.665	3.562	4.075	4.067	-1.337	-0.280
1Mn 2×2×1 (NM)	3.755	4.121	4.232	4.156	5.077	7.959
1Mn 2×2×1 (PM)	2.923	3.289	3.400	3.324	2.913	5.794
2Mn 2×2×1 (NM)	3.609	4.556	4.362	4.195	3.425	4.368
2Mn 2×2×1 (PM)	3.463	4.410	4.217	4.050	-1.223	-0.279
1Mn 2×2×2 (NM)	3.844	3.145	4.890	4.600	5.296	10.337
1Mn 2×2×2 (PM)	3.012	2.313	4.058	3.768	3.131	8.172
2Mn 2×2×2 (NM)	3.646	4.094	4.736	4.494	3.891	6.703
2Mn 2×2×2 (PM)	3.500	3.949	4.591	4.349	-0.757	2.055

5. Conclusions

From the experimental and calculated results presented in this paper, the following conclusions can be drawn: (1) the paramagnetic (PM) character of the austenite phase has important consequences for the ability of oxide complexes present in the steel to absorb elements like Mn and Ti present in the steel; (2) in addition to MnS precipitation along the peripheries of the complex inclusions, Mn can be absorbed by TiO_x and MgTiO_x ; (3) Mn atoms in the steel matrix can also be absorbed by MgO, unless when Ti is present in the melt, since then absorption of Ti is more likely than that of Mn. The Mn atoms absorbed by MgTi_2O_4 and MgTiO_3 , occupy Mg sites in the crystal structure. Mn atoms from the steel matrix cannot be absorbed by Al_2O_3 . MgAl_2O_4 only has very weak ability to absorb Mn atoms; (4) absorption of

dispersed Mn atoms in the steel by Ti_2O_3 is associated with a change in crystal structure resulting in the formation of stable Mn-Ti complex oxides or occurs by Mn occupying vacancy positions in the Ti_2O_3 crystal. Absorption of dispersed Mn atoms in the steel by Ti_3O_5 occurs through the formation of a new stable Mn-Ti complex oxide or by the transformation of Ti_3O_5 to Ti_2O_3 oxides that absorb Mn.

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