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Relation between oxygen activity gradient in the internal oxidation zone of Mn alloyed steel and the composition of oxide precipitates

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ABSTRACT

An internal oxidation zone with $(Mn_{1-x},Fe_x)O$ mixed oxide precipitates occurs after annealing a Fe – 1.7 at.% Mn steel at 950 °C in N_2 plus 5 vol% H_2 gas mixture with dew point of 10 °C. Local thermodynamic equilibrium in the internal oxidation zone is established during annealing of the Mn alloyed steel. As a result, the composition of $(Mn_{1-x},Fe_x)O$ precipitates depends on the local oxygen activity. The oxygen activity decreases as a function of depth below steel surface, and consequently the concentration of Fe decreases in the $(Mn_{1-x},Fe_x)O$ precipitates.

Mn is one of the major alloying elements in advanced high strength steels, which are used for automotive applications to reduce the weight of car bodies and thereby reducing fuel consumption and CO_2 emissions. To protect these steels against corrosion a zinc coating is applied, usually by hot-dip galvanizing. However, during annealing of these steels prior to galvanizing the Mn can be oxidized easily, which may impair the zinc coating adhesion [1]. Then, it is beneficial if the oxides are formed beneath rather than at the steel surface.

The kinetics of internal oxidation of Fe-Mn binary steel alloys has been studied experimentally [2] and a numerical model has been developed to simulate the internal oxidation behaviour of Fe-Mn binary alloys [2,3]. Extension of this model to simulate internal oxidation of multi-element alloyed steels has also been reported [3,4]. A vital assumption in all internal oxidation models [2,3,5], as in the model adopted here [2], is that local thermodynamic equilibrium is reached between dissolved oxygen, alloying elements, iron matrix and oxide precipitates. However, experimental proof for the establishment of local thermodynamic equilibrium inside alloy matrix during internal oxidation of Mn alloyed steels is lacking. In this work, it will be shown from the observed composition depth profile of the internal oxide precipitates formed during internal oxidation of Mn alloyed steel that local thermodynamic equilibrium indeed occurs.

FeO and MnO, which are known as Wüstite and manganosite respectively, have the same rock salt crystal structure. Hence, FeO and MnO can form a continuous solid solution also known as manganowüstite, henceforth denoted as $(Mn_{1-x},Fe_x)O$; see e.g. [6]. When annealing steels alloyed with Mn, $(Mn_{1-x},Fe_x)O$ mixed oxide can be formed at the steel surface even below the dissociation oxygen partial pressure of FeO [7]. The concentration of Fe-ions dissolved in the external $(Mn_{1-x},Fe_x)O$ increases with dew point (i.e. oxygen partial pressure) in the annealing atmosphere [7]. When these Mn steel alloys are oxidized internally, $(Mn_{1-x},Fe_x)O$ precipitates are formed in the internal oxidation zone (IOZ). However, the composition of these precipitates depends on the local activity (i.e. chemical potential) of dissolved oxygen. Upon internal oxidation a gradient of oxygen activity in the IOZ exists which results in the inward diffusion of dissolved oxygen. Hence, if local thermodynamic equilibrium between dissolved oxygen and oxide precipitates is established, it is expected that the concentration of Fe in the $(Mn_{1-x},Fe_x)O$ decreases with depth.

In this work, the concentration and activity depth profiles of dissolved oxygen are predicted quantitatively for steels alloyed with Mn using a numerical internal-oxidation simulation tool [2]. Since the thermodynamic data of the Fe-Mn-O ternary system have been well assessed in the currently available thermodynamic databases [8], the corresponding composition of the internal $(Mn_{1-x},Fe_x)O$ as a function of depth is calculated using a thermodynamic computation tool [9]. The actual composition depth profile of the internal oxide precipitates is determined experimentally from their lattice parameter as obtained from X-ray diffractometry (XRD).

The steel alloyed with 1.7 at.% Mn were annealed for 1 h at 950 °C in N_2 + 5 vol% H_2 gas mixture at a dew point of 10 °C, corresponding with an oxygen partial pressure of 2.3×10^{-17}. This dew point was realized

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by adding de-aerated and deionized water vapour to the gas flow of 1500 sccm passing through a 30 mm inner diameter quartz tube in a horizontal furnace (Carbolite MTF 12/38/850, UK). Based on the fluctuation of the dew point during annealing observed with a cooled mirror analyzer (Optidew, Michell Instruments, UK), the uncertainty of the dew point in the annealing atmosphere is about 2 °C. The annealing process is terminated by moving the steel sample to the cold zone of the quartz tube, allowing the steel sample to be cooled down to room temperature. The cooling rate from the annealing temperature to about 400 °C is about 180 °C/min. Further details of the experimental setup are described elsewhere [2]. Under these annealing conditions internal oxidation of Mn alloyed steel will prevail [10]. The composition of the steel used is: 0.48 at.% C, 1.72 at.% Mn, 0.097 at.% Si, 0.004 at.% Al and balance Fe.

To obtain the composition depth profile of internal $(Mn_{1-x},Fe_x)O$ with X-ray diffractometry (XRD), the surface of sample after annealing was mechanically polished to remove a layer with certain thickness. The polishing was done with 1 μm diamond grains using a soft cloth (Lam Plan MM431, UK). After each polishing step the sample was thoroughly cleaned ultrasonically with isopropanol. The thickness of the surface layer removed was determined from the measured weight loss of the sample after polishing and considering the polished surface area. For the density of the steel 7.87 g/cm^3 is taken. The sample was weighted with an analytical balance (Mettler M5SA, Switzerland) having an accuracy of ± 10 μg.

After each polishing step, the lattice constant of the $(Mn_{1-x},Fe_x)O$ precipitates in the alloy matrix was determined from XRD measurements. XRD patterns were recorded with a Bruker D8 Discover diffractometer in the grazing incidence geometry using Co $K\alpha$ radiation, in the 2θ region between 37° and 57° with a step size of 0.01° 2θ and a dwell time of 30 s. The incidence angle of the X-ray beam was fixed at 3° with respect to the sample surface. As the analysis depth, the depth below the surface corresponding with 70% of the diffracted intensity of pure iron was taken, which is 1.27 to 1.34 μm [11] for 2θ from 30° to 60°. The data evaluation was done with the Bruker software Diffrac.EVA version 4.0. The position of the (111) and (200) diffraction lines of $(Mn_{1-x},Fe_x)O$ was determined by fitting a parabola to the top of the diffracted intensity peak after smoothing and stripping $K\alpha_2$ contribution [12]. The peak positions were corrected for instrumental errors by measuring reference SRM LaB$_6$ 660 [13] on a (510)-Si wafer using the same acquisition parameters as used for the sample, except that the dwell time per step was 1 s.

The (111) and (200) peak positions determined of the $(Mn_{1-x},Fe_x)O$ precipitates were also corrected for any residual stress, as determined by the so-called $\sin^2\psi$-method [11].

The composition of $(Mn_{1-x},Fe_x)O$ formed in a Fe-Mn binary alloy in thermodynamic equilibrium with a gaseous oxidizing environment as a function of oxygen partial pressure at 850, 950 and 1050 °C is presented in Fig. 1(a). This diagram was calculated using Factsage [9] by considering thermodynamic equilibrium between a Fe-Mn alloy, $(Mn_{1-x},Fe_x)O$ and a gas mixture of $Ar + O_2$ at atmospheric pressure. First, the thermodynamic data for the solid solution oxide $(Mn_{1-x},Fe_x)O$ was taken from the FToxid database [8]. Then, a gas mixture of Ar and O_2 with a total pressure of 1 atm at different oxygen partial pressures was created with thermodynamic data from the FactPS database [8]. Finally, a solid solution of Fe-Mn binary alloy with fcc crystal lattice was created with the thermodynamic data in the FSstel database [8].

Since MnO is more stable than FeO, the dissociation oxygen partial pressure of MnO is lower than that of FeO. Below the dissociation oxygen partial pressure of MnO, Fe and Mn form a solid solution. Above the dissociation oxygen partial pressure of MnO, $(Mn_{1-x},Fe_x)O$ mixed oxide is formed and the concentration of Fe dissolved in the $(Mn_{1-x},Fe_x)O$ increases with the ambient oxygen partial pressure. Above the dissociation oxygen partial pressure of FeO the entire alloy phase will oxidize and hence the concentration of Fe in $(Mn_{1-x},Fe_x)O$ is constant. The dissociation oxygen partial pressure of both MnO and FeO increases with temperature; see Fig. 1(b). Between the dissociation oxygen partial pressures of MnO and FeO, the concentration of Fe in the $(Mn_{1-x},Fe_x)O$ decreases with temperature. Increasing Mn concentration in the Fe-Mn alloy from 1.0 to 2.5 at.% has a negligible effect on the Fe concentration in $(Mn_{1-x},Fe_x)O$. Also, the Fe concentration in $(Mn_{1-x},Fe_x)O$ is practically independent of the crystal lattice of the Fe-Mn alloy phase (i.e. ferrite or austenite).

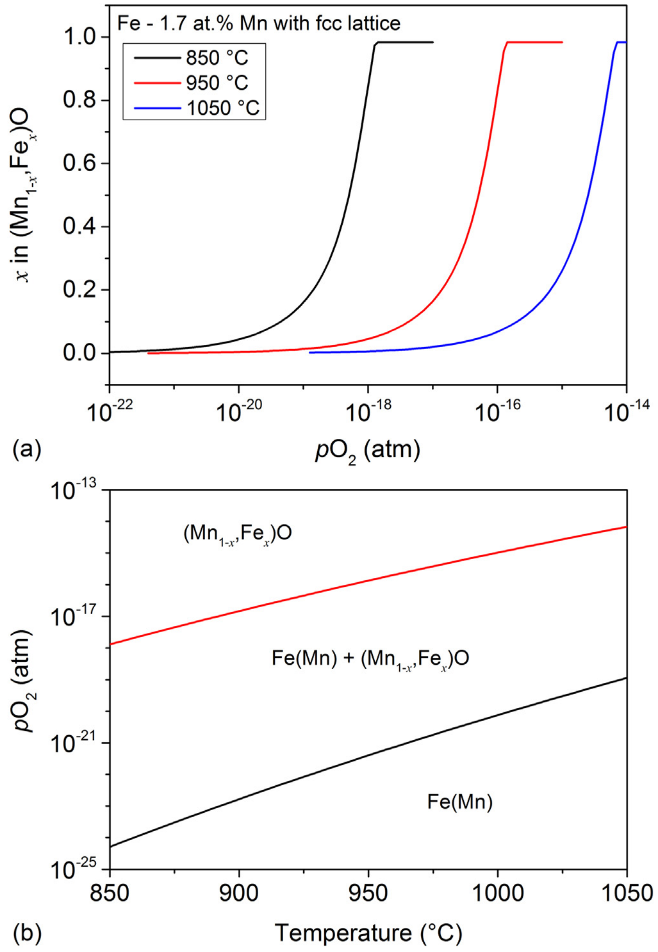

Fig. 1. (a) Computed Fe concentration in $(Mn_{1-x},Fe_x)O$ mixed oxide as a function of oxygen partial pressure (logarithm scale) at 850, 950 and 1050 °C in the Fe-Mn alloys with fcc crystal lattice at thermodynamic equilibrium with oxidizing gas atmosphere; (b) computed phase diagram of Fe – 1.7 at.% Mn alloy with fcc crystal lattice in oxidizing gas atmosphere, black and red lines represent the dissociation oxygen partial pressure of MnO and FeO, respectively.

The concentration depth profiles of dissolved oxygen in the IOZ of steels alloyed with 1.0, 1.7 and 2.5 at.% Mn after annealing at 950 °C in a gas mixture of N_2 plus 5 vol% H_2 with a dew point of 10 °C were calculated using a finite difference method considering the precipitation of oxides [2]. At 950 °C the mole fraction of dissolved oxygen at steel surface in equilibrium with the gas mixture of N_2 plus 5 vol% H_2 with a dew point of 10 °C is about 3.6×10^{-6} [7]. For the diffusion coefficient of oxygen a value of 3.5×10^{-7} cm^2/s [14] was adopted. As can be seen in Fig. 2(a), the concentration of dissolved oxygen decreases almost linearly with depth. The concentration of dissolved oxygen at internal oxidation front is practically zero. Since the depth of IOZ decreases with the bulk Mn concentration in the alloy, the concentration gradient of dissolved oxygen across the IOZ increases with the Mn concentration in the base alloy under the same ambient oxygen partial pressure.

Yet, the composition depth profile of $(Mn_{1-x},Fe_x)O$ internal precipitates can be calculated using the thermodynamic tool [9] considering local thermodynamic equilibrium with the dissolved oxygen. To this