Effect of a grain-refined microalloyed steel substrate on the formation mechanism of a tight oxide scale

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Keywords
substrate, oxide, steel, scale, microalloyed, refined, grain, formation, effect, tight, mechanism

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Effect of a grain-refined microalloyed steel substrate on the formation mechanism of a tight oxide scale

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Abstract

The formation mechanism of tight oxide scale on the microalloyed steel was investigated at temperatures of 550 to 850 °C in dry air. Microstructural characterisations reveal that the spallation of oxide scale dominates at the centre of coarse grains on the oxidation initiation. The fine-grained steel improves the adhesive properties of oxide scale by enhanced grain-boundary diffusion. The lower activation energy and higher oxidation rate accelerate cation/anion migration along grain boundaries, leading to high magnetite content in the oxide scale. The approach by grain refinement at initial oxidation has been proposed to generate the pickle-free tight oxide scale.

Keywords: Microalloyed steel, Oxide scale; Magnetite; High temperature oxidation
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1 Introduction

As-hot-rolled microalloyed steels exhibit nearly doubled in strength while still maintaining adequate toughness, weldability, ductility and formability, and thereby offer a great potential to further substitute conventional quenched and tempered steels [1, 2]. The improvement of the toughness and weldability can be obtained by the reduction of carbon content, and the resultant decrease in strength is compensated by the additions of Si and Mn [3]. Much higher strength can be enhanced through precipitation hardening and fine grained hardening by microalloying with low cost Nb, V, and Ti, individually or complexly [4]. Nowadays, the as-hot-rolled high strength steels have found extensive applications in various structures and automotive components.

Promising potential for the automotive microalloyed steel lies in the pickle-free tight oxide scale formed on the surface of hot-rolled strips due to thermal oxidation at elevated temperatures [5]. The tight oxide scale is expected to deform with steel substrate without cracking, and may act as lubricant between the workpiece and tool during downstream processing. Our previous work [6, 7] indicated that tribological properties of the oxide scale could be enhanced by the presence of magnetite precipitates due to their decreased hardness, preferable ductility and adhesive ability. The proposed oxide scale comprises of more than 75 % magnetite and retained wustite, with the oxide-layer thickness of less than 15 μm. The tight oxide scale obtained can be applied directly to the stamping process after hot rolling.

The processing time during the finishing hot rolling and subsequent laminar cooling would be
significantly shortened at relatively high cooling rates as the process conditions are modified. Due to the natural difference of thermal properties between oxide scale and steel substrate [8], the resultant high cooling rates will inevitably cause adhesive properties of the tight oxide scale to deteriorate. It is widely accepted that a range of possible adhesive-related failure modes (spallation and buckling) can occur during cooling process, and some of these are dependent on the interfacial properties between the thermally grown oxide scale and steel substrate [9, 10]. The interfacial fracture can be triggered possibly due to the local properties variations including the morphological features and the thickness of oxide scale, chemical compositions and roughness at the oxide/steel interface [11, 12]. Particularly, the presence of a few amounts of various alloying elements has made an understanding of the overall situation elusive [13, 14].

To develop the mechanism responsible for this tight oxide scale, it is necessary to investigate the effect of the steel substrate on the oxidation initiation. The integrity of the oxide scale is largely affected by growth stresses which developed within the oxide scale during the oxidation process, and also by the residual stresses that result after cooling to room temperature [15, 16]. Surface oxide cracking associated with oxidation-induced grain boundary sliding at the oxidation temperature occurs in response to the evolving compressive growth stress in the oxide scale [17]. Different mechanism for the spallation failures resulted from these stresses have been preferred as possible explanations. One of the most influential ideas is that elemental oxygen penetrates the grain boundary at or ahead of surface cracking, reduces cohesion and thereby accelerates cracks growth [18]. During the initial stage of oxidation when a continuous thin layer formed, some studies [19] found that the critical concentration of alloying elements could be a function of the grain size of steel substrate. Grain refinement of steel substrate influenced the resulting oxide composition and morphology, and thereby altered the oxidation behaviour [20-23]. Coarse-grained steels grow
alloying-rich oxides over the steel grain boundaries and Fe-rich oxides over the steel grains, whereas, the fine-grained steels form a uniform alloying-rich oxide [24]. Several studies [25-27] have found that the adhesive-related failure normally appears on the centre of grains of steels, while it disappears in the vicinity of the grain boundaries due to the accumulation of alloying elements there. Additionally, the additions of small amounts of Cr are known to be another major cause of the improvement in adhesion properties [26]. During the early stage oxidation, oxygen diffuses into the steel substrate and reacts with solute elements which are more oxygen active than the base steel [27, 28]. The formed oxides phase could act as a diffusion barrier and improve the scale adhesion.

However, a coherent understanding of how grain size influences specific oxide structures when they are desired is largely lacking. Since coarsening of the grains would take place at high temperatures, less works to date have been reported on effects of the temperature-dependent grain coarsening on the oxidation initiation. There has been limited work on the formation mechanisms of tight oxide scale on the Nb-V-Ti microalloyed low carbon steel during early stage oxidation and subsequent cooling process. The facile and controlled microstructure of the desired magnetite phase has not been well explored, which is therefore of fundamental and practical interest.

In this present work, we intend to characterise the initial oxidation behaviour of fine-grained Nb-V-Ti microalloyed steel in a wide range of temperatures under dry air, thereby to establish the constitutive relationship between the grain size of the steel substrate and that of the corresponding oxide scale. This investigation also extends upon previous experiments [6] in which a new three-layer microstructure of the oxide scale has been presented. Having this target microstructure, this paper will try to find what type of the steel substrate can generate this oxide scale, and further
to delve the mechanism of their formation. On the basis of the results of these earlier experiments, together with additional experiments described in the current work, an advantageous and facile approach using grain refinement of the steel substrate at initial oxidation was proposed to increase the magnetite content to form the pickle-free tight oxide scale.

2. Experimental

2.1 Material and sample preparation

The material used was a commercial low-carbon Nb-V-Ti microalloyed steel for an automotive beam. The chemical compositions of the studied samples are tabulated in Table 1. In order to fit into the heating stage sample holder, metal coupons containing the crucible with the external diameter of 5 mm and the inner diameter of 4 mm was used for the high temperature oxidation for in situ exposures. The steel samples were sectioned into 2.7 mm × 2.7 mm × 2 mm thick pieces using a Struers Accutom-50 cutting machine. One of the broad faces on the samples was ground using SiC papers of 2400 mesh to a surface finish of 0.6 µm. Prior to the experiments, the samples were cleaned in ethanol using ultrasonic agitation and then stored in a desiccator.

In addition, the dilatometry tests were carried out to determine dynamic continuous cooling transformation of the microalloyed steel, and the obtained austenitisation starting and finishing temperatures can be applied into the initial oxidation tests during heat treatment cycles. The dilatometry samples were 10 mm long hollow cylinders with a 5 mm diameter and 0.75 mm wall thickness, and were machined from the 5 mm microalloyed plate.
2.2 Apparatus and oxidation procedure

In situ investigation of initial oxidation behaviour of the microalloyed steel was performed on a laser scanning confocal microscope (LSCM-VL2000DX, Lasertec in Yokohama) equipped with an ellipsoidal infrared image furnace (Model SVF17SP, Lasertec), and with a CCD camera as a detector [29]. The heating system consisted of a 1.5 kW halogen lamp positioned in the lower focal point of a small gold-plated ellipsoidal chamber that reflected the light to the other focus point where the sample was positioned. Thermocouples incorporated around the sample holder were used to determine and control the temperature by a digital PID controller (ES100P, Omron). Ultra high purity Ar passed through a chamber with Ti turnings at 850°C. A real time oxidation video from a CCD light detector was connected to a computer at a rate of 25 frames per second, for later editing. Once a polished sample in the 4 mm diameter aluminium crucible was inserted into the LSCM chamber, the oxidation of the steel is observed in situ and recorded following a preselected annealing programme.

The initial oxidation tests of the microalloyed steel were conducted at the temperatures of 550, 600, 750, and 850°C. The following procedure was used for each oxidation experiment: (1) the sample was heated to 1050°C at a rate of 1.7°C/s under a high purity argon atmosphere, and held for about 5 min to homogenise the austenite grains; (2) the sample was then cooled to the desired temperatures at a rate of 1.7°C/s and held for 0.5-2 min; (3) the protective gas was switched to industry-purity air at the desired flow rate for a duration of 30 s at a constant temperature; (4) the oxidation gas was switched off and (5) high purity argon was switched back to prevent further
oxidation, and then the sample was cooled to room temperature at a rate of 1.7 \( ^\circ \text{C/s} \). This heat-treatment schedule is illustrated schematically in Fig. 1. It should be noted that the oxidation time was based on the industrial hot rolling process. The total time for the formation of tertiary oxide scale was 26 s measured by a steel factory. Therefore, an exposure time of 30 s was used in the present oxidation experiments.

During the oxidation tests, an industrial compressed air was used as the dry oxidising gas. A stainless steel tube with the diameter of 3 mm was positioned on top of the sample holder so that the oxidising gas was directly injected onto the surface of the polished sample. By blowing air directly onto the specimen surface, the influence of a varying oxygen partial pressure on the kinetics of oxidation is minimised [29]. It is therefore more likely that the specimen surface would be exposed to an instantaneous and constant partial pressure of oxygen of 0.21 atm during oxidation. The compressed air was introduced at a constant flow rate of \( 3.1 \times 10^{-5} \text{ m}^3/\text{s} \), rendering a velocity of 12 m/s. The flow rate of the inert gas was varied between \( 6 \times 10^{-6} \) and \( 5 \times 10^{-5} \text{ m}^3/\text{s} \).

Additionally, the dilatometry tests were conducted in a Theta II high speed thermo-mechanical simulator. The specimens were heated to the temperature of 1200 \( ^\circ \text{C} \) at a heating rate of 20 \( ^\circ \text{C/s} \), held for 180 s to dissolve microalloyed carbides, and then cooled to room temperature at different rates.

2.3 Analysis methodology
The surface topography after oxidation was immediately examined in a Nanoscope IIIA atomic force microscope (AFM) in order to prevent the surface of the sample from being contaminated after each oxidation experiment. Several images were recorded at different locations for all samples to verify the reproducibility of the observed features. Then Au deposition, the samples were coated in epoxy resin to protect the oxide scale. For cross-sectional analysis, the edges of the sample were ground on 2000 grit SiC paper, and ion-milled at 6 kV for 5 h using a Ticix 020 Leica cross-sectional ion miller [30]. A JEOL-JSM 6490 scanning electron microscope (SEM) and An XT Nova Nanolab 2000 focus ion beam (FIB) microscope were used to investigate the surface morphology, microstructures and the thickness of the oxide scale. These measurements for the thickness of the oxide scale can be used to define oxidation kinetics based on image analysis. A GBC MMA diffractometer with mono-chromated Cu-Kα radiation was used to detect the phase composition of the samples after oxidation. The steel substrates were also mapped from the mid-planes of the samples using a field emission gun scanning electron microscope (FIB-SEM) equipped with an Oxford Instruments Channel-5 electron back-scattering diffraction (EBSD) system operating at 15 kV with a step size of 0.125 µm.

3. Results

3.1 Characterisation of the microalloyed steel

Prior to the oxidation experiments, the properties of the microalloyed steel substrate were analysed. Fig. 2 shows a typical dilatation vs. temperature curve of the steel specimens at the heating rate of 20 °C /s. Dynamic continuous cooling transformation diagram (CCT) of a Nb-V-Ti microalloyed steel which has similar chemical compositions to the steel applied in the current study is also
presented in Fig. 2 [2]. The specimen contracts during heating although the increase of temperature as a result of the microstructure rearrangement during phase transformation [31]. From this curve in Fig. 2a, the starting and finishing of phase transformation can be easily detected, where $A_{c1}$ and $A_{c3}$ are 725 and 865 °C, respectively. Further previous experiments [2] indicate that the transformation zone of ferrite and pearlite is about 550-750 °C and the transformation zone of bainite is about 410-580 °C. The martensite can hardly generate at cooling rate lower than 40 °C/s due to the low carbon and microalloyed design. The dilatation tests provide that the studied steel has broad process window to produce the ferrite-pearlite steel or ferrite-bainite steel.

Fig. 3 presents typical optical microscope (OM) and SEM images of the surface morphology of the etched microalloyed steel using 2 % nital solution for 20 s. The microstructure of steel substrate consists of 94 % fine-grained polygonal ferrite and 6 % perlite at a cooling rate of 20 °C/s and a cooling temperature of 660 °C. The grain size of the polygonal ferrite was determined as 3 µm by using circular intercept method according to ASTM: E112-10. The fine and dispersive pearlite are in the matrix of ferrite. High magnification SEM image (Fig. 3b) indicates that most of fine-grained ferrite in the microalloyed steel, where the bright line in Fig. 3b refers the grain boundaries in the steel substrate.

3.2 Microstructural characterisation

3.2.1 In situ oxidation observation
Fig. 4 provides a series of in situ frames from the first 30 s of the oxidation experiments in industrial dry air at 550 °C, showing the initial formation and growth of oxide scale on the surface of the sample. The colour on the surface of the sample changed as the oxidation time proceeded. This may be due to variations in the thickness of the oxide scale, but other factors such as different oxide orientation and surface conditions can also affect the colour change. Fig. 4a shows the microstructure of the sample that was heated to 1050 °C under argon seal and held for 5 min. Since the starting temperature in the austenite single phase zone, the microstructure is the pan-caked austenite due to heavy deformed in the austenite unrecrystallization zone. The microstructure of the sample before air was introduced in Fig. 4c includes the clear grain boundaries of initial austenite. It is evident from Fig. 4d that oxidation initially took place at the grain boundaries after the oxidising gas exposure. The oxide scale spread rapidly over the steel substrate and the colour in the grains changed, as shown in Fig. 4d. As the oxidation time proceeded by 1 s (Fig. 4e), the oxide scale continued to grow, but it took about 30 s for a complete oxide scale to form, which is similar to the formation of tertiary oxide scale. The oxide scale after cooling in protective gas for 39 s (Fig. 4f), where the obvious boundaries can be observed as the oxide scale shrunk.

The cause to present the oxidation at 550 °C is based on a previous study [22, 32]. Generally, it was hard to detect the oxide growth at this temperature in dry air where magnetite is stable. Similar oxidation behaviours were observed at temperatures of 600, 750 and 850 °C. The oxide scale that formed during cooling in a protective atmosphere also shows the surface of the sample contracting, whereas at 750 °C there was only slight contraction due to rapid oxidation. With an increase of the oxidation temperature, the growth rates of the oxide scale increased significantly, so no more than 1 s was required for the oxide scale to cover the whole sample surface. It is noted that the surface
grain size of the steel substrate has no dramatic change below 1050 °C [33, 34]. This allows the grain growth mostly occurs during recovery and recrystallization [35, 36]. Therefore, the selection of the different starting cooling temperatures aims to obtain spatial non-uniformity in the matrix grain size.

3.2.2 Surface morphology and cross section characterisation

Fig. 5 presents the surface morphology of the formed oxide scale after oxidation tests at temperatures of 550, 600, 750 and 850 °C. The dashed lines marked indicate that the grains of the steel substrate and formed oxide share the same ridges. At 550 °C (Fig. 5a), less surface roughened other than along the grain boundaries, which indicates a minor oxidation occurred. These protrusions were sparsely observed along certain boundaries on the uniform surface of the oxidised samples at 600 °C (Fig. 5b). Although the surface morphology oxidised at 750 °C (Fig. 5c) becomes more homogenous, there are much higher oxides protruding from the grain boundaries, and some pores and micro-cracks also dispersed on the entire region. This could be attributed to the rapid oxidation at 750 °C and the accumulation of thermal stress caused by the subsequent cooling after oxidation process. Fig. 5d shows the surface oxides developed at 850 °C has regions of localised spallation and blistering failure. High magnification SEM images in Fig. 5e and f show that the spalling of oxide scale occurred at the centre of grains of the microalloyed steel substrate after oxidation at 850 °C. It is clearly seen that the grain boundaries of the steel substrate under the debris of oxide scale (Fig. 5f). This shows that the regions with different growth rates are related to the oxidation originating from the central of metal grains or at grain boundaries [29]. The
relationship between different growth rates and the locations of the underlying grains could be seen in all the exposed environments. In the temperature range of 550 and 750 °C, the transformation of ferrite and pearlite in the microalloyed steel could occur as indicated by the results from dilatometry tests described above. Since it has been widely reported [11, 37-39] that the phase composition of oxide scale is more important than the thickness for the integrity of an oxide layer, the results described here provide another possibility for dissecting the adherence properties of oxide scale associated with the grains size of the microalloyed steel substrate as a result from oxidation temperatures.

In cross section, the tight oxide scale has different morphologies formed on the fine-grained (Fig. 6a) and coarse-grained steel substrates (Fig. 6b). For the fine-grained steel substrate, the oxide scale appeared uniformed in morphology, which is well adherent to the homogeneous grains of the steel substrate (Fig. 6a). While the oxide scale developed on the coarse-grained steel has regions of localised spallation failure, which is prominent when covering the non-uniformed grains of the steel substrate (Fig. 6b). Therefore, the homogeneous grains of the steel substrate can possibly enhance the potential contribution of grain-boundary diffusion to the integrity of the oxide scale [40, 41]. These results suggest that the adhesive failure at the steel/oxide interface could be caused by the compressive stress within the intergranular oxide scale sparsely formed on the coarse-grain steel substrate during the cooling process. Specifically, a representative EBSD grain size map for the steel substrate after oxidation at 850 °C (Fig. 6c) shows the grain size of the polygonal ferrite is about 10-20 µm, where grain size with large grains in red, small in blue. Here the distribution of grain size in the outer layer is much non-uniform than that of in the inner layer across the cross section. The spatial non-homogeneity of the grain size could cause adhesion properties of oxide scale to deteriorate. Further, the distribution of grain boundaries of the steel substrate in Fig. 6d
indicates the presence of high-angle grain boundaries, which could have significant effects on the oxidation rate of the steel substrate. This will be discussed in Section 4.1.

In addition, the cross-sectional characterisation of oxidised samples aims to further determine the mechanism of steel/oxide separation occurring at the interface itself (adhesive failure) or near it (cohesive failure) [42]. SEM images of FIB cross sections in Fig. 7 show the morphologies of oxide scale developed on the steel substrate at 550 and 600 °C in dry air. Many failures at 550 °C (Fig. 7a) are really cohesive in the oxide near the interface and involve oxide growth stresses, oxide and metal plasticity and thermal cycling effects due to differential thermal contraction. By contrast, adhesive failures appeared at 600 °C (Fig. 7b) relate to interfacial energy, and can affect the steady-state interface morphology, varying from impurity segregation and even the physical contact at asperities. Therefore, these results indicate the oxide scale formed at 550 °C depends significantly on the growth stress, mechanical properties of oxide scale and heat treatment, whereas, the oxide scale at 600 °C depends on alloying element accumulated and surface topography of the steel substrate. It suggests that the major effect properties of the oxide scale and the corresponding steel substrate has on the integrity of oxide scale. These features of the oxide failure described above mean that the separation stress within the oxide scale is less than the separation stress at the oxide/steel interface at temperature up to the 550 °C, and exceeded above 600 °C (Fig. 7c). This result extends the adhesive properties of oxide scale at temperatures range of 850-870 °C during the FEM modelling assumption [11]. These stresses cause behind could be due to the volume changes associated with phase transformation in the steel substrate while heating or cooling the samples, which can lead to separation stresses in the oxide scale.
3.2.3 Surface topography

In order to quantify the surface roughness of the oxidised samples, the surface topography was measured. Fig. 8 shows the AFM images of the surface topography of the samples after 30 s oxidation at temperatures of 550 and 600 °C in air. At 550 °C, the surface of sample shows mild oxidisation with a relative smooth surface topography, as shown in Fig. 8a. Further oxidation at 600 °C results in the oxides protruding from the surface (Fig. 8b). It can be seen that the roughness of the surface increased significantly at higher temperatures, which suggests that the oxidation temperature exerts considerable influence on the oxidised surface topography of the microalloyed steel. It also indicates that a very low surface roughness value could be obtained with a lower oxidation temperature and a shorter exposure time in the air.

3.3 X-ray structural analysis

After in situ analysis of high temperature oxidation, the oxide scale generated at the temperatures of 550, 600 and 750 °C were detected using x-ray diffraction technique at room temperature, as shown in Fig. 9. The composition of oxide scale is consistent with the expected oxidation behaviour at the intermediate temperature. The predominant oxide is magnetite with smaller amounts of sparse hematite and ferrite during the early oxidation stage. The variation of oxidation temperature has significantly influence on the phase composition of oxide scale, particularly, in the case of multiple oxide phases formed at the temperature of 750 °C. Nevertheless, it can be noted that there is few retain wustite phase as a product of initial oxidation, which indicates that the decomposition of
wustite could be completed at this intermediate temperature. This is possibly due to that the high density of the grain boundaries of the steel substrate causes the diffusion of cation/anion ions to take place the phase transition $\text{Fe}_{1-x}\text{O} \rightarrow \text{Fe}_3\text{O}_4$.

4. Discussion

4.1 Initiation of oxidation mechanism

The oxidation rate can be expressed by the slope of the curve plotting the measured thickness of the oxide scale versus oxidation time based on SEM cross sectional image analysis. In this case, the variation in oxidation rates among the specimens is the greatest during the early stage, with the highest rates generally corresponding to the specimen with the largest grain size. Fig. 10 is an Arrhenius plot of the parabolic oxidation rate constants drawn from the oxidation of the low carbon steel [41] and the microalloyed steel in this experiment. The equation for the solid line is,

$$k_p = \frac{A}{T^n}$$

where a least squares calculation of $k_p$ values for the fine-grained microalloyed steel. The data points of the steel substrate at 850 $\degree$C were excluded because of the structural irregularities in the oxide scale (Fig. 5) caused by the oxide/metal separation under the cooling process. The data given by the solid line are therefore considered to truly represent the growth of uniform, adherent, and multi-phased FeO-Fe$_3$O$_4$-Fe$_2$O$_3$ oxide scale on the fine grained steel substrate. It is noted that the
The absence of wustite below 570 °C could affect the variation of the overall oxidation rate. The previous calculations [43, 44] show that the reason for the decrease in the oxidation rate of Fe-Cu alloys with respect to pure iron is related to the practical disappearance of wustite from the oxide scales.

The dot line in Fig. 10 is the least squares solution for $k_p$,

where scattered value drawn from Ref [41] for the low carbon steel. The data of the dot line have appreciably different activation energies, possibly because of poorer adhesion properties in oxide scale, although this could not be confirmed from their publication. The higher $k_p$ values and the slightly lower activation energy in solid line reflect the finer grain size of the initial formed oxide and the fact that cations diffuse preferentially along grain boundaries.

Compared the parabolic rate constants of previous studies [41, 45-48] with the present work, the solid line signified the current study lies along the upper limit of the spread of $k_p$ values for the dot line. The activation energy of 179.2 kJ/mol corresponds closely to that of iron reported 194.9 kJ/mol (46.6 kcal/mol) between 640 and 805 °C [45]. Further, the lower value of activation energy exactly approximates to that 174.5 kJ/mol for Fe in the Fe grain boundaries diffusion between 530 and 650 °C [49]. According to Fisher’s model, enhanced element migration occurred in the grain
boundary domains assuming a thickness of 50 nm [50]. This value corresponds to the thickness of the experimentally observed grain boundary oxides. It is known that the activation energy for grain-boundary diffusion decrease with increasing grain-boundary energy [51]. This kind of high-angle grain boundaries in Fig. 6d with higher energy might be especially helpful for grain boundary diffusion. Therefore, the smaller grain size and the higher grain-boundary energy can play an important role in increasing the effective diffusion coefficient of iron-ions and oxygen in steel substrate at intermediate temperature as a result of grain-boundary diffusion. In this investigation, the higher rate constants and the lower activation energy are considered to be the fine-grained steel substrate which accelerates preferential diffusion along grain boundaries during the early stage oxidation.

4.2 Effect grain refinement of the steel substrate on tight oxide scale

4.2.1 Magnetite formation

Enhanced grain-boundary diffusion in the initial oxidation suggests that decreasing the grain size of the steel substrate could alter the diffusion process, and thereby to change the overall composition of oxide scale, which could be responsible for high desired magnetite content (more than 75 %) in the proposed tight oxide scale. The fine-grained steel substrate has a large number of grain boundaries serve as ‘short-circuit’ channels for ions diffusion in the early stage oxidation [13, 20, 52-54]. The inward diffusion of oxygen along the grain boundaries can be involved as a result of rapid grain-boundary diffusion through the oxide scale and the enhanced solid solubility of oxygen in the steel substrate. By this mechanism, the oxide scale is believed to grown on both sides: the reaction of iron-ions and oxygen at the oxide/air interface and the reaction of oxygen with the steel
substrate near the oxide/steel interface. So there exists much more oxygen-rich layer (magnetite phase) in the fine-grained substrate than that in the coarse grained steel.

Moreover, metal and oxygen react to form a thin layer of oxide scale whose composition more-or-less mirrors the compositions of the steel substrate as the short-time oxidation during hot rolling. The alloying elements contained, such as manganese, chromium and silicon, could contribute to the early stage oxidation similar to those discussed in detail in Refs. [55-58]. It is believed that selective oxidation of manganese and chromium occurred at grain boundaries on the surface [57], or dispersed all the cross-section oxide scale [57, 58], even further to lower the wustite point [56]. Normally, silicon was observed accumulating at the oxide scale/steel interface [10, 59]. In any case, the transport of these ions is generally via lattice or grain boundary diffusion [13]. Therefore, the increase of diffusion paths as the decrease of the grain size could enhance the accumulation of these alloying elements at the grain boundaries.

To further interpret these, the role of grain-boundary diffusion can be illustrated using a mathematical model with a corresponding effective-diffusivity coefficient of the species ($D_{\text{eff}}$),

where $D_L$ and $D_{GB}$ are the diffusion coefficients in the lattice and along the grain boundaries, respectively, and $f$ is the area proportion of grain boundary. Assuming that grains have the shape of spheres or cubes, the volume fraction of interfaces $f$ may be estimated as $2\delta/d$ (where $\delta$ is
grain-boundary width and \( d \) is the average grain diameter. The grain-boundary width \( \delta \) is of the order of an interatomic distance and \( \delta \sim 0.5 \) nm is a widely accepted value \[50, 53, 54\]. Since \( D_{\text{GB}} >> D_L \) in most cases, Eq. 3 can be simplified as,

If the grain size \( d \) is very small, the \( D_{\text{eff}} \) is dominated by the second term on the right side of the equation. The increase of the \( D_{\text{eff}} \) thus depends on the relative magnitude of \( D_L \) and \( D_{\text{GB}} \), and the temperature dependence of \( D_L \) and \( D_{\text{GB}} \). Normally, grain-boundary diffusion has smaller activation energy than lattice diffusion, so that the ratio \( D_{\text{GB}}/D_L \) decreases as the temperature increase \[50\]. Therefore, \( D_{\text{eff}} \) increases dramatically with a decrease of \( d \) at intermediate temperatures. If assuming as the effective diffusivity of ions in the coarse-grained \( (d = 10 \mu\text{m}) \), Fig. 11 illustrates the ratio of \( D_{\text{eff}} \) is enhanced by grain refinement. For instance, if \( d \) is reduced from the reference 10 \( \mu\text{m} \) to 3 \( \mu\text{m} \) in this work, \( D_{\text{eff}} \) is about 1 order of magnitude larger than that of in the case of \( D_{\text{GB}}/D_L = 10^2 \), and over 2 orders of magnitude larger when \( D_{\text{GB}}/D_L \) equals \( 10^3 \) and \( 10^6 \).

4.2.2 Adhesion properties

Surface spallation failure did not occur on the fine-gained steel oxidised at 550 and 600 °C (Fig. 5a, b), whereas, the oxide scale which formed on the coarse-grained steel at 850 °C was often buckled between grains of the steel substrate (Fig. 5e) during cooling to room temperature. Two
factors can account for the difference: first, the grain size of oxides is limited by the smaller grain size of the steel substrate, and is therefore sufficiently small to allow plastic deformation; secondly, the more numerous steel grain boundaries provide enough vacancy sinks to suppress spallation formation. Even though no clear trend or relationship has apparently been established between the grain size of the metal and that of the corresponding oxide scale, the oxide scale growth on fine-grain materials also tends to have smaller oxide grains [28]. In our experiments, some of these processes were underway during the initial oxidation period.

It should be pointed out here that the failure of the oxide scale is connected with the grain size non-uniformity of the corresponding steel substrate. The spallation of oxide scale corresponding to the coarse-grained surface at 850 °C (Fig. 5e) was found in some regions, whereas other regions were covered by the tight oxide scale formed on fine grained substrate (Fig. 5d). Another type of microstructural non-uniformity occurred in the cross section of the steel substrate (Fig. 6b), where indicated the formation of coarse-grained zones arranged in the outer layer of the steel substrate. Whatever the type, microstructure non-uniformity of the steel substrate is detrimental to adhesion properties of oxide scale, and should be avoided. A spatial non-homogeneity of the grain development could be a result of either non-uniformity in the matrix grain size or non-uniformity in the particle distribution or both of them [60]. The heat treatment is normally characterised by strain non-homogeneity across the cross section with the strain being greater in the outer layer. In any case, the data presented here could be related to the above types of microstructural non-uniformity.

Oxide/steel interface failures at 550 °C were really cohesive in the oxide near the interface, whereas, adhesive failures appeared at 600 °C at the oxide/steel interface (Fig. 7). This result further implies the steel substrate has significant influence on the integrity of the oxide scale and the mechanism of
steel/oxide separation. Based on these findings, grain refinement effect of the steel substrate on adhesive properties was proposed to reveal spallation and formation mechanism of the tight oxide scale, as schematically shown in Fig.12. The higher concentration gradient of the ions diffusion in the coarse-grained steel appears at the grain boundaries, which result in the non-uniform oxidation over the entire surface of the steel substrate (Fig.12a). The oxide scale generated on the coarse-grains steel substrate thereby leads to the non-homogenous compressive stress. The residual stress can be relived during the subsequent cooling process and further some spallation failure observed on the steel substrate at room temperature (Fig.12b). In comparison with coarse-grained steel, the intergranular oxide scale formed on the fine-grained steel can act as a wedge when cooling to the room temperature (Fig.12d). As such, homogenous compressive stress can be dispersed in uniform oxide scale formed.

In addition to grain size of the steel substrate, different phase microstructures [48] could be another trigger to cause adhesion properties of the oxide scale to deteriorate. From dynamic continuous cooling transformation diagram [2] (Fig. 2b), the microstructure of steel substrate consists of ferrite and pearlite at a cooling rate of 1.7 °C/s and a starting cooling temperature of 550 and 600 °C in this study. The duration, i.e. the holding time 2 min and the following 30 s oxidation in Fig. 1, is much longer than the incubation time 100 s in Fig. 2b, to allow phase transformation of the steel substrate. While, the steel substrate starting cooling from 750 and 850 °C is in the austenite single phase zone in Fig. 2b. Therefore, the variation in diffusion rates of cation/anion ions through austenite and ferrite matrix [13, 21, 29] could have a certain effect on the initial oxidation process, and on the adhesion properties of the formed oxide scale.
In addition, the type of crystallographic surface also significantly affects the final topographies of oxide scale. The grain orientation of metal substrate has previously been proposed to affect the oxide growth at 350 °C [61]. It was found that the growth of oxides on a single crystal (001) surface was much faster than that on a single crystal (112) surface. It is therefore plausible to predict a similar effect could be exerted on the initial oxidation of microalloyed steel in this study, leading to the variation of adhesion properties.

5. Conclusions

Initial oxidation behaviour of the microalloyed steel was investigated through austenitising at 1050 °C then cooling to 550, 600, 750 and 850 °C by 1.7 °C/s, and following 30 s oxidation in dry air. A formation mechanism of the tight oxide scale was proposed to elucidate effects of grain refinement in the steel substrate on high desired magnetite content and the integrity of the oxide scale. The following conclusions can be drawn in this present work.

1. The surface spallation failure of oxide scale occurred at the centre of grains of the microalloyed steel substrate on the oxidation initiation. The oxide scale grown on the coarse-grain steel substrate can cause adhesive properties to deteriorate when cooling to the room temperature. This grain refinement effect is more sensitive to the oxide scale formed at 550 °C than that formed at 600 °C.

2. High and uniform magnetite content obtained in the proposed tight oxide scale could attribute to enhanced grain-boundary diffusion as a result of increasing high density of the grain boundaries of the fine-grained steel substrate. The higher values of oxidation rate constant and the slightly lower
activation energy provide compelling evidence that the initial oxide scale grows on both cation/anion ions migration along oxide grain boundaries.

3. The advantageous approach by grain refinement at initial oxidation was proposed to increase the magnetite content to form the pickle-free tight oxide scale, which is promising potential for the application of the automotive microalloyed steel.

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References


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Figure captions

**Fig. 1** Schematic illustration of the heat-treatment schedule used for in situ oxidation test.

**Fig. 2** (a) Dilatation versus temperature curve of the steel specimens at the heating rate of 20 °C/s. $A_{c1}$ and $A_{c3}$ are austenitisation starting and finishing temperatures during heating. (b) Dynamic continuous cooling transformation diagram of the Nb-V-Ti microalloyed steel [2], austenite (A), ferrite (F), pearlite (P) and bainite (B).

**Fig. 3** (a) OM microstructure of the microalloyed steel substrate showing polygonal ferrite and pearlite, (b) SEM image for surface morphology of the polygonal ferrite.

**Fig. 4** Snapshots from video recorded an in situ for the formation and growth of oxide scale on the surface of the specimen for 30 s oxidation in dry air, (a) austenitising of steel substrate at 1050 °C, (b) at 850 °C, (c) transformed phase of steel substrate, (d) introduction of oxidising gas at 550 °C, (e) in oxidation process, and (f) the oxide scale under the protective gas cooling. The time indicated in the figure is the program proceeding time rather than oxidation time.

**Fig. 5** SEM images of the oxidised samples after 30 s exposure to dry air at (a) 550 °C, (b) 600 °C, (c) 750 °C, (d) 850 °C, (e) spallation of oxide scale occurred at the centre of grains of the microalloyed steel substrate after oxidation at 850 °C, (f) enlarge image of (e), where the dashed lines mark the ridge boundaries of the steel substrates.

**Fig. 6** Cross sections of tight oxide scale formed on (a) fine-grained and (b) coarse-grained steel substrate. (c) Representative EBSD grain size map for the steel substrate after oxidation at 850 °C, (d) Histogram of grain boundaries of the steel substrate.
**Fig. 7** SEM images of FIB cross sections showing morphology of oxide scale developed on the steel substrate at (a) 550 °C, and (b) 600 °C. (c) Schematic representation of the effect of temperature on the stresses separating the oxide scale and steel substrate; data from the literature [11] is added for comparison.

**Fig. 8** AFM images of the surface topography after 30 s oxidation at different temperatures in air, (a) 550 °C, (b) 600 °C.

**Fig. 9** X-ray diffraction patterns of oxide scale formed at (a) 750 °C, (b) 600 °C, and (c) 550 °C.

**Fig. 10** Arrhenius plot of final parabolic rate constant. Activation energy for growth of uniform, adherent polycrystalline oxide scale (solid line) is 179.2 kJ/mol; data from the literature [41] is added for comparison. (It is noted that the bottom $X_1$ axis corresponds to the top $X_2$ axis using the equation $X_2=1000/X_1-273.15$.)

**Fig. 11** Relationship between the effective diffusivity ratio $D_{\text{eff}}/D_{\text{eff}}^*$ and the grain size of the steel substrate $d$, where the reference one $D_{\text{eff}}^*$ with the grain size of 10 µm. This demonstrates that $D_{\text{eff}}$ is enhanced by grain refinement.

**Fig. 12** Schematic diagram of spalling mechanism of oxide scale, (a) the oxide scale formed on coarse-grained steel substrate, (b) spallation failure by compressive stress when cooling, (c) the oxide scale formed on fine-grained steel substrate, (d) the formation of the tight oxide scale when cooling down to room temperature.
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<th>P</th>
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