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Tribological properties of magnetite precipitate from oxide scale in hot-rolled microalloyed steel

Xianglong Yu
University of Wollongong, xly991@uowmail.edu.au

Zhengyi Jiang
University of Wollongong, jiang@uow.edu.au

Dongbin Wei
University of Wollongong, dwei@uow.edu.au

Cunlong Zhou
Taiyuan University of Science and Technology, China, zcunlong@163.com

Qingxue Huang
Taiyuan University of Science and Technology, China

See next page for additional authors

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Abstract

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Keywords

rolled, microalloyed, steel, precipitate, magnetite, tribological, oxide, scale, properties, hot

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Authors

Xianglong Yu, Zhengyi Jiang, Dongbin Wei, Cunlong Zhou, Qingxue Huang, and Daijun Yang

Tribological properties of magnetite precipitate from oxide scale in hot-rolled microalloyed steel

Xianglong Yu [a], Zhengyi Jiang [a,*], Dongbin Wei [a], Cunlong Zhou [b] and Daijun Yang [c]

[a] School of Mechanical, Materials and Mechatronic Engineering, University of Wollongong, Wollongong NSW 2522, Australia

[b] School of Materials Science and Engineering, Taiyuan University of Science and Technology, Shanxi, 030024, China

[3]Shougang Research Institute of Technology, Shougang Group, Beijing, 100043, China

*Corresponding author: Z.Y. Jiang; Tel: 61 2 4221 4545; Fax: 61 2 42215474; Email: jiang@uow.edu.au

Abstract

Nano-magnetite (Fe_3O_4) particles have a potential to lead to the formation of lubrication tribofilm that reduces the friction and wear in hot steel strip rolling. In this paper, an attempt to fabricate the oxide film with magnetite precipitates from thermally-grown wustite ($Fe_{1-x}O$) layer during isothermal cooling of low carbon microalloyed steel, was obtained. The precipitation behaviors were investigated on Gleeble 3500 thermo-mechanical simulator under the humid air with water vapour content of 19.5 vol.%. Several types of magnetite precipitates were examined using scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD) analysis. The tribological properties of magnetite precipitates were investigated in pin-on-disc configuration. It found that the disperse magnetite particles originate from either the pro-eutectoid precipitation above 570°C or the partial decomposition of wustite below 570°C. The oxide film on the presence of free particles during eutectoid precipitation could be a lubricant and consequently resist wear, particularly for the oxide scale with a typical thickness in the range of 8 to 11μm in dry air and moisture atmosphere. Furthermore, characterisation and precipitation process of the oxide scale are discussed, with respect to a probable mechanism to explain the lubricated properties has been proposed.

Keywords: Wear, Friction, Hot-rolled steel, Oxide scale, Magnetite precipitation

1. Introduction

The addition of nano-magnetite (Fe_3O_4) particles offers a great potential as lubricant additives or for the development of advance lubrication technology [1, 2]. Generally, the three oxide phases generated during hot rolling for low carbon steel, wustite (approximate composition $Fe_{1-x}O$), magnetite (Fe_3O_4) and hematite (α-Fe_2O_3) have the cubic sodium chloride, the spinel and the rhomboedral type of structures [3], respectively. Wustite and magnetite are more ductile and show a better wear resistance. However, wustite is thermodynamically unstable and subjected to become fragile at ambient temperature, in contrast to the tribological properties of high temperature [4, 5]. Hematite α-Fe_2O_3 with a high hardness is known to present an abrasive behaviour which increases friction and wear. Additionally, hematite α-Fe_2O_3 is easy for spallation during coiling or annealing after laminar cooling in hot rolling due to a lack of crystal continuity when grains of the rhomboedral hematite grow based on the cubic spinel magnetite. Kim et al [3] examined the grain growth of the interface between hematite and magnetite, and confirmed that the hematite grains grow at an angle of 60 degrees from the <100> crystal direction of magnetite.

Consequently, it is anticipated, after hot rolling, to develop the oxide scale consisted of the appreciable amounts of magnetite particles, which achieves a decreased hardness, preferable ductility and adhesive ability at room temperature. After that, this type of oxide scale formed on steel strip, through cold rolling without acid pickling, can deform with the steel substrate absent from cracking, spallation and other surface failures. First of all, these oxide particles in the oxide scale are expected as natural lubricant additives which may facilitate to form a lubrication tribofilm reducing friction and wear during cold steel rolling.

Nevertheless, the thermally grown oxide scales exhibit various morphologies and characteristics after hot rolling [6]. The final properties of oxide scale formed on the steel strip depend significantly on phase composition and microstructures of the tertiary oxide scale generated at finishing temperature, particularly the phase transformation among iron oxides in laminar cooling and coiling processes [6, 7]. Conventionally, the tertiary oxide scale is composed of three well defined layers, a thick wustite $Fe_{1-x}O$ layer adjacent to the steel substrate, then an intermediate magnetite Fe_3O_4 layer, and finally a thin outermost hematite Fe_2O_3 layer [6, 8]. The same three layers structure is maintained until a eutectoid point of Fe-O system (Fig. 1) [9], about

570°C is reached, following by a series of equilibrium transformations, mainly the eutectoid precipitation of magnetite particles from the wustite layer.

According to the decomposition mechanism of wustite at different temperature ranges, the magnetite precipitation is largely classified into the high-temperature pro-eutectoid above 570°C and the partial eutectoid transformation below 570°C, as shown regions A and B in Fig. 1. As for temperatures during laminar cooling after hot rolling, this study focuses on the eutectoid reaction below 570°C. The precipitating magnetite particles depend appreciably on the transformation temperature, the cooling rate and the chemical composition of steel substrates. More particularly, magnetite precipitates are initially generated from wustite decomposition to develop a continuous layer at the interface of oxide scale/steel substrate in the temperature range of 370 and 470°C, which is called magnetite seam [6]. Besides, previous hypothesis [10] has been proposed that the oxide scale with the magnetite seam has good adhesive properties under stresses conditions at ambient temperature.

Therefore, to generate a specific oxide scale, and then to study the tribological behaviour of the oxide scale are focused in this study. Naturally, it is necessary to obtain the oxide scale with a desirable amount of magnetite precipitates, which contribute to natural lubrication additives during the following cold rolling. Correspondingly, the aim of this study is to reproduce the specific type of the oxide scale during the hot rolling and then to simulate the friction evolution of magnetite particles in the oxide scale during cold rolling process. Consequently, the oxidation experiments were carried out on a Gleeble 3500 thermal-mechanical simulator, with which a humid air generator has been developed for using the humid air atmosphere. The tribological properties of magnetite precipitates have been investigated using a pin-on-disc configuration on a CETR UMT multi-specimen test system. The precipitation characteristics of magnetite particles after oxidation were examined by scanning electron microscope (SEM) in conjunction with energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD) analysis. Two types of steel surfaces were investigated in the simulation of friction tests, one is a fresh metallic surface and the other is an oxidised surface. The testing parameters such as the shear strength of oxide scale, surface roughness of strip were measured at different testing conditions to investigate the tribological behaviours. Additionally, a probable lubrication mechanism of magnetite particles was discussed based on the contribution of microalloying elements.

2. Experimental

2. 1 Materials

The material used in the oxidation experiment was commercial hot-rolled strips from low carbon microalloyed steel for automotive beam provided by a steel plant, China. Mechanical properties for the grade of steel are shown in Table 1. In a pin-on-disc configuration, the pin consists of a roll material and the disc consists of a steel strip with the specific thickness and composition of oxide scale after oxidation treatments. The main chemical composition of the samples is given in Table 2.

2. 2 Oxidation test

The low carbon microalloyed steel materials used in this investigation were cut into specimens with the size of 120×25×5mm^3 for the oxidation tests. The surface finish of the manufactured specimens is average roughness *Ra* 0.6μm. Before tests, the specimen surface was ground using SiC paper of 2400 mesh to remove the existing thin oxide protective film, degreased in an ultrasonic cleaner, washed in water, ethanol then dried immediately.

Oxidation tests in a short time in the humid air were conducted using Gleeble 3500 thermo-mechanical simulator. In the case of the moist atmosphere, the controllable moisture was obtained by passing industrial air through a distilled water tank which was maintained at a constant temperature. More generally, the water vapour contents between 7.0 and 19.5 vol.% in humid air are relevant to hot rolling of plain carbon steel [11, 12]. During laminar cooling after hot rolling process, the steel strip through the last stands is subject to a majority of cycling water for cooling down to coiling temperature. That is why in this oxidation tests, the water vapour content in humid air was set as 19.5 vol.%. Attention must be paid that before the oxidation experiments the gas tube connecting the water tank and the Gleeble chamber must be pre-heated to prevent the condensation of water on the inside diameter of the tube.

The specimens were oxidised at 800°C for 120s in 19.5% H_2O moist air, through a desired cooling rate and then held at 550°C for 30-120min in argon seal, as shown in Fig. 2. The following procedure was used for each of the oxidation experiments: (1) the sample was heated to the austenitising temperature of 900°C in an argon protective atmosphere at a heating rate of 10°C/s; (2) holding for 20s at 900°C, argon was switched off and the oxidising atmosphere introduced, while the temperature was decreased to 800°C; (3) then, the sample was cooled down to 550°C in moist atmosphere, where humid air was released and kept flowing into Gleeble chamber in $1.7\times10^{-4}m^3/s$ for 120s; (4) after holding for 30-300min at 550°C, the sample was quenched to room temperature at 40°C/s, and the argon flow was switched on to prevent any further oxidation during the isothermal treatment.

In the oxidation experiment, different methods were used to protect the integrity of oxide scales. Uniform oxide scales were consistently obtained at each experiment for 19.5% water moist atmosphere. Firstly, during the cooling process in Gleeble 3500, a rapid cooling rate around 40°C/s was selected to down to room temperature, after that the sample was took out from the chamber to pre-mounting using epoxy-resin. Therefore, the procedure avoids the blistering or other failures of oxide scale due to the steep temperature gradient. Secondly, a modified pre-mounting procedure was followed [13]. After the good mixing of the epoxy resin and the hardener, leave there for a while until the liquid more viscous, when it is going to be solidified, just at this time, spread this thick paste onto the surface of the oxide scale. On the one hand, under this situation there is no any liquid to flow all around. On the other hand, it is an effective measure to avoid the non-uniform contraction between the liquid resin and the solid oxide scale during the solidification of the resin. These prepared samples would be used to the subsequent tribological test.

2.3 Tribological test

Tribological tests were carried out under a pin-on-disc configuration on a CETR UMT multi-specimen test system [14-17] as shown in Fig. 3a. In this case, the shape of the pin was a high chrome steel ball with 6.35 mm diameter. The microstructure of the pin made of tempered martensite and cementite presents an initial hardness of 67 HRC (or 890 HV) and a roughness Ra of 0.24±0.04µm. The chemical composition of this pin is given in Table 2. The grade of the disc, a strip material, is low carbon microalloyed steel shown in Table 2, with an initial hardness of 162Hv and a roughness Ra of 0.04±0.02μm. Two types of different surface morphologies for strip materials were investigated in the experiment. One is a relatively fresh metallic surface, the other is an oxidised surface with the steel surface oxidised at 800°C for 120s in 19.5% H_2O moist air and then held at 550°C for 60min in argon seal. The same procedure as the sample preparation in the oxidation test was applied to obtain the fresh surfaces of steel. These samples were sectioned into the size of 20×24mm^2 using a Struers Accutom-50 cutting machine. In the case of pre-mounting oxidised samples, it is necessary to cut a sample from the middle part around the welding position of the thermal couple [7], where the oxidised surface was absent from the steep thermal gradient during oxidation process. Subsequently, each sample was cold mounted in a stainless steel stub with an inner diameter of 50mm, as shown in Fig. 3b, and positioned as central in this ring as possible. The purpose of the cold mounting is to meet the specified size requirement of the lower sample holder on the pin-on-disc apparatus employed in this experiment. The steel surfaces of the solidified-resin-mounted samples were polished to 1μm. And the other oxidised surfaces were reserved. Eventually, the opposite surface of the sample was flattened to obtain the specific thickness of the sample with the parallelism tolerance of 6μm between the top and the bottom surfaces. It is noted that in this study the thickness of sample is 14mm when the resin is 50g with 6g harder during cold mounting. Three samples with different oxidised precipitation surfaces and two samples with fresh metallic surfaces were prepared to the friction test. One of oxidised samples is shown in Fig. 3b.

The operating conditions applied for each friction test are: (1) a normal load of 2.4, 8 and 18N, (2) a linear sliding speed of 0.05, 0.15 and 0.35ms^{-1}. In order to obtain a sufficient pressure of contact with a low normal load, the pin shape presents a hemispherical surface of contact area. For a load ranging from 2.5 to 20 N, the hertzian pressures vary from 130 to 280 MPa at the start of the friction test. All the tests were conducted at a room temperature of about 20°C, so that different precipitations of oxide scale formed in hot rolling were used to examine the effects on cold rolling at room temperature. A Coulomb-type coefficient of friction was recorded in situ from a strain gauge sensor during the experiments. This coefficient corresponds to the ratio of macroscopic forces which are the resistant force to the motion and the normal force applied on the pin [18]. A stylus-type Hommel Tester T1000 profilometer with ISO11562 filter was employed to measure the surface roughness of samples. The test conditions were selected relatively soft regions in order to observe the tribological behaviour of oxide scales in the contact zone without destroying them too fast. For each test condition, three tests have been carried out in order to verify the reproducibility of the results.

After each friction test, the surfaces of all the samples were coated with gold for 10-15s using a sputter coater. A JEOL JSM 6490 scanning electron microscope (SEM) in conjunction with energy dispersive spectroscopy (EDS) analysis was employed to examine the precipitation morphology and the microstructures of oxide scale formed on the sample surface, and to investigate the worn surfaces. Moreover, the thickness of the oxide scale was also measured through observed cross section of oxidised samples. An X-ray diffraction (XRD) using a GBC MMA diffractometer with monochromated Cu Kα radiation was used to analyse the phase composition of the oxide scale.

Actually the operating conditions of friction tests are rather different from the industrial rolling conditions. Nevertheless, he aim of this study is not to simulate the hot rolling process but to reproduce a part of the contact mechanics established between the strip with a certain composition of the oxide scale and the working roll used in the finishing stands in the first step of process. The mechanical contact of a typical rolling bite is decomposed: only the sliding part of the motion is considered, the rolling part of the motion being neglected. Further, the tribological configuration of contact in this study: a sliding motion with an initial hertzian pressure close to the contact pressure in the rolling bite, allows us to display impact of the composition of oxides on friction and wear mechanisms. In the present paper, only the results with a normal force of 18N and a linear sliding speed of $0.35ms^{-1}$ are emphasised. Nevertheless, the phenomena observed in the present case remain valid for the other test conditions.

3. Results and discussion

3. 1 Precipitation behavior of magnetite

Fig. 4 shows the cross section of oxide scales after oxidation in Gleeble 3500 thermo-mechanical simulator at 800°C for 120 s in dry air and 19.5% water moist atmosphere then held at 550°C for 60min. It can be seen that the eutectoid layer in the two-layer oxide structure is precipitated evenly in dry air but not with moist air. The oxide scale formed in the dry air has a less compact structure and a clear interface with the substrate as shown in Fig. 4a. The oxide scale formed in 19.5% water moisture however shows a thin and compact magnetite seam adhering to the steel substrate as shown in Fig. 4b.

Fig. 5 compares the thickness of oxide scales across the width of oxidised specimens formed under two different atmosphere conditions at 800°C and held at 550°C for 120min. It is evident that the thickness of oxide scale is in the range of 8-11μm, which is relatively thinner at the center of specimens than that near edge region in both dry and moist atmospheres. Moreover, the oxide scale formed in 19.5% H_2O moisture air is always thicker than that in dry air. It indicates that the oxidation rate is more rapid in moist air than in dry air for the type of low carbon microalloyed steel.

Fig. 6 shows the XRD results of oxidised surface at 800°C in dry industrial air for different holding time at 550°C. It can be found that the main phases in oxide scale are Fe_3O_4 and Fe_2O_3. As the tests were carried out directly on the oxidised surface and X-ray went through the oxide scale and reached the metallic phase, the Fe phase appears in the XRD results. Subsequently, since the oxide scale layer is getting thicker with time, the intensity of Fe phase's peak should be reduced with the oxidation time. On the contrary, the intensity of Fe phase's peak shows no sign of decrease with the oxidation time. That is because the eutectoid reaction, $4FeO \rightarrow \alpha\text{-}Fe + Fe_3O_4$, occurred during holding time at 550°C.

Fig. 7 shows the XRD results of oxidised surface at 800°C in 19.5% H_2O moisture air for different holding time at 550°C. It can be seen that the oxide scale consists mainly of Fe_3O_4 and Fe_2O_3. The constitution of Fe_2O_3 decreases with holding time. It can be explained that the formed oxide scale under the moist conditions is non-uniform structure as shown in Fig. 4b, and thus it is much easier for Fe_2O_3 to spall from the Fe_3O_4 surface during the preparation of samples.

It is note that the thin outermost Fe_2O_3 phase is detected by XRD in Figs. 6-7, compared with that of absence from SEM photographs in Fig. 4. Generally, the crystal structure of Fe_2O_3 [3] and the different sample preparations for XRD and SEM, result in the difference of Fe_2O_3 content. Nevertheless, in the industrial hot rolling which belongs to a short-time oxidation, the effect of Fe_2O_3 can be neglected because the red dust (Fe_2O_3) nearly has been flushed away through online cooling and then coiling after hot rolling.

3. 2 Tribological properties of magnetite precipitates

Fig. 8a shows the original morphology of the sample surface with globular precipitation of magnetite particles on the wustite surface during the isothermal treatments at 550°C for holding 60 min. It can be seen that small magnetite precipitates as free particles disperse over the whole wustite suface after the oxidation test. These free magnetite particles [19, 20] could contribute to be a lubricant and consequently protective against wear when the oxides enter into the contact between the work rolls and the strip. It is noted that in the EDS analysis (Fig. 8b) most of the intensity is Fe and O, no other alloying elements be observed.

Fig. 9a illustrates the coarse lamellar precipitation of magnetite particles formed on the wustite surface during the isothermal treatments at 550°C for holding 120 min. It can be seen that the aptitude of magnetite precipitates are coarsely compacted into the surface. When the compact surface of oxide scales occurred in the contact between the work roll and the steel strip until the formation of glased surfaces, the predominant mechanism of wear could become adhesion and the coefficient of friction could be increase [21]. As for the coarse lamellar structure, the filling of the irregularities and the bigger volume occupied by the oxide with regard to the healthy metal, contributes to the roughness increase [22]. It is interesting to note that the manganese element was also detected in this precipitation surface (Fig. 9b), which could confirm alloying elements go into solid solution of the oxide scale formed on this kind of steel surface, and thus to improve the crystal continuity [3]. The fact that silicon oxides and other alloying element oxides were not detected may be due to a small percentage of these products compared to the whole oxide phases.

Fig. 10a shows the fine lamellar precipitation of magnetite particles formed on the wustite surface during the isothermal treatments at 550°C for holding 300 min. It can be seen that the morphology surface is very similar to the coarse lamellar structure shown in Fig. 9. That is because, from the coarse lamellar to the fine lamellar structure, the eutectoid reaction, $4FeO \rightarrow \alpha\text{-}Fe + Fe_3O_4$, only involves the growth of precipitation grains, whereas there is no other new products generated [3]. This microstructure of magnetite precipitation could be easy to form glased surfaces when the contact between the work roll and the steel strip. In this case, the decrease in the coefficient of friction could be because the fine lamellar structure has a smoothing of the interface as the thickness of the oxide scale [22].

The correlation between the sliding speed and the coefficient of friction was summarised in Fig. 11, which is the fine lamellar structure, a typical occurrence for the precipitation of magnetite phase, under the conditions of the normal force 18N and dry air flow between surfaces. The points plotted are the means of at least three tests, provided with the standard deviation in Fig. 11. It can be seen that the coefficient of friction at the high speed presents relatively low, the oxides due to friction heat and favour an adhesive wear. However, there is a minimum coefficient of friction for this case. Low sliding speeds could make easy the formation of thicker, and thus affect wear resistance. Therefore, it is implied that there is also minimum thickness of oxide scale to perform lubrication [22].

For the case of friction test with oxidised surfaces, the propagation of the cracks in the bulk under shearing stresses may cause the detachment of oxide scales at the pin contact surface [23, 24]. The shear strength of oxide scale is defined as the maximal interfacial shear stress [25], where an interfacial fracture will be triggered on the oxide and steel substrate interface. In this study, the shear strength for oxide scale detachment is determined based on image analysis technique [26]. Fig. 12 shows the correlation between the roughness at interface steel/oxide scale and the shear strength of the oxide scale. As shown in Fig. 12, with Ra-values up to 0.38μm only a slight influence to the scale shear strength is observed, whereas with higher roughness values (Ra>0.38μm) the shear strength increases significantly. It indicates that there is a minimum value for shear strength of oxide scale, where the oxide scale has strong adherence to the steel substrate.

3.3 Formation mechanism of magnetite precipitates

Therefore, in order to fabricate the oxide scale with a desirable amount of magnetite precipitates after hot rolling contribute to natural lubricate additives during the following cold rolling, the real challenge is to clarify the formation mechanism of the specific oxide scale. For the case of oxidised surfaces holding at 550°C, the reaction belongs to the decomposition of the thermally grown wustite, which is the solution of ferric ions, rather than the oxygen diffusion during high temperature oxidation [8]. Initially, some magnetite particles generate from the wustite layer above 570°C, which indicates the following decomposition corresponding to the area A in Fig. 1.

$$Fe_{1-x}O \rightarrow vFe_{1-y}O + (1-v)Fe_3O_4{}^{\mathrm{I}}. \quad (1)$$

where $x>y$, $Fe_{1-y}O$ is an iron-rich wustite, $v=(1-4y)/(1-4x)$, $Fe_3O_4{}^{I}$ is the primary magnetite. Whereas below 570°C the low-temperature decomposition as shown in the region B in Fig. 1, the initial wustite is decomposed into metastable stoichiometric wustite (enriched with iron) and oxygen-rich wustite $x>z$.

$$Fe_{1-z}O \rightarrow FeO + Fe_{1-x}O \quad (2)$$

Then, the decomposition of oxygen-rich wustite into stoichiometric wustite and the secondary magnetite:

$$Fe_{1-x}O \rightarrow vFeO + (1-v)Fe_3O_4{}^{II} \quad (3)$$

where Eq. (1) is true, when y = 0. Finally, the breakdown of metastable stoichiometric wustite into two equilibrium phases:

$$4FeO \rightarrow \alpha - Fe + Fe_3O_4{}^{III} \quad (4)$$

where $Fe_3O_4{}^{III}$ is the tertiary magnetite.

Reaction Eq. (3) proceeds rapidly and exceeds reaction Eq. (4) to a considerable extent at temperature of maximum decomposition rate in area B (250 to 350°C) [6] in several hours, with the probable result of more observed magnetite precipitates than ferrite.

Fig. 13 presents the Fe_3O_4 precipitating structure from oxide scales formed on the contact surfaces during friction tests, which is probable to have the desirable tribological properties for cold rolling. In this case, it is supposed to be pre-oxidised FeO on the substrate in Fig. 13a. On the one hand, some Fe_3O_4 particles appear on the surface of FeO layer (Fig. 13a) due to further oxidation, on the other hand, the proeutectoid Fe_3O_4 (Fig. 13b) also occurs and depletes some oxygen within the FeO. In Fig. 13c, the oxidised Fe_3O_4 nucleates into a thin film, whereas some eutectoid structures, Fe_3O_4 and α-Fe, exhibit at the site of proeutectoid products. Since the eutectoid reactions lead to the depleted oxygen near the outer layer, Fe_3O_4 particles start to precipitate at the interface of FeO and the substrate. Eventually, a typical three-layer eutectoid structure of oxide scale generated: the outer layer of Fe_3O_4 film with the relatively decreased hardness, then the eutectoid structure composed of α-Fe, Fe_3O_4 and retained FeO with preferable ductility, the inner layer of Fe_3O_4 seam with desirable adhesive ability to the steel substrate.

A large number of friction tests and stalled cold rolling experiments will need to be carried out to investigate the evolution of steel surface morphology and roughness in moist air, and eventually the wear mechanics of magnetite precipitates. The oxidation test on the Gleeble thermal mechanical simulator and tribological test in pin-on-disc configuration provide the framework for future studies to assess the tribological characteristics of magnetite precipitates.

4. Conclusions

The following conclusions can be made according to the oxidation tests under dry and moist (19.5% H_2O) atmospheres of a low carbon microalloyed material. The oxide scale consists mainly of Fe_3O_4 and Fe_2O_3 owing to the instability of FeO at ambient temperature. Water content has a significant influence on the precipitation behaviour of Fe_3O_4 from thermally grown FeO. Moisture atmosphere not only increases the thickness of oxide scale, but also influences the microstructure and morphology of Fe_3O_4 precipitation within the oxide scale. The formed oxide scale exhibits a thin compact Fe_3O_4 seam adjacent to the steel substrate, which is absent from that with dry air.

During the tribological tests, the microstructure and mechanical properties of Fe_3O_4 precipitation and the friction conditions have been investigated. Two types of Fe_3O_4 precipitates, globular or lamellar structure have been developed for tribological experiment. The experimental results indicate the two types of precipitation structure exhibit quite different tribological behaviors. The free particles in the globular structure could contribute to be a lubricant and consequently resist wear, whereas the compact particles in the lamellar structure may favor an adhesive wear. The link between lamellar structure and adhesive wear depends on the type of lamellar structure. The fine lamellar structure has a smoothing of the contact interface, thus the coefficient of friction decreases, whereas the coarse lamellar structure with the irregularities leads to the roughness increase. The investigation into the effect of the sliding speed and the shear strength on friction shows that there is a critical thickness of oxide scale for optimum lubrication, which shows that the oxide scale has strong adherence to steel substrate.

Eventually, the evolution mechanism of magnetite precipitates within oxide scale has been clarified with respect to the defined primary, secondary and tertiary Fe_3O_4 precipitates. A new three-layer microstructure of Fe_3O_4 precipitation has been presented: the outer Fe_3O_4 film with decreased hardness, then the eutectoid products layer with certain ductility, and the Fe_3O_4 seam with desirable adhesion to the steel substrate.

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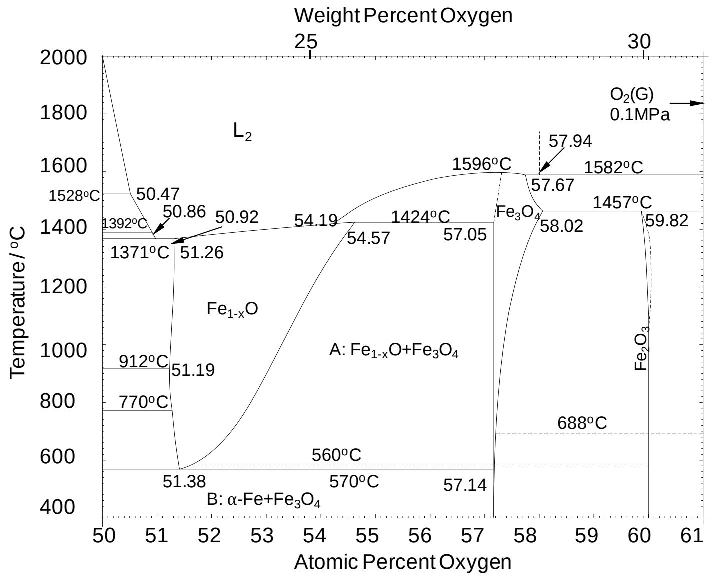

Fig. 1 Fe-O equilibrium phase diagram [9]. Region A: high-temperature pro-eutectoid above 570°C, region B: wustite decomposition below 570°C

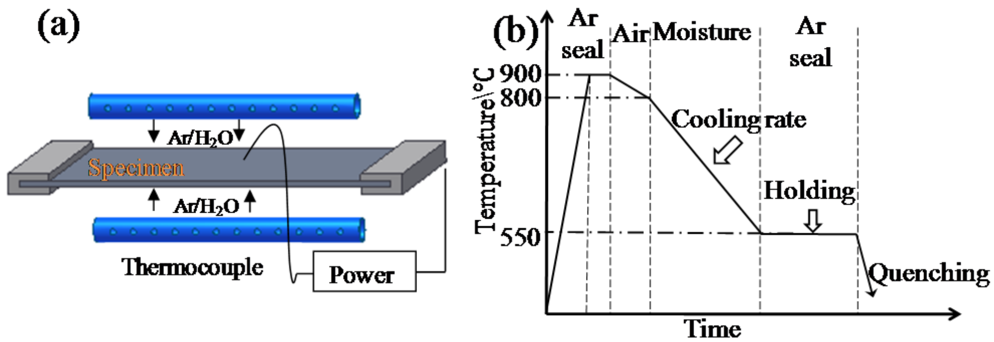

Fig. 2 High temperature oxidation in Gleeble 3500, a) illustration of sample setup, b) thermo-cycle for oxidation test

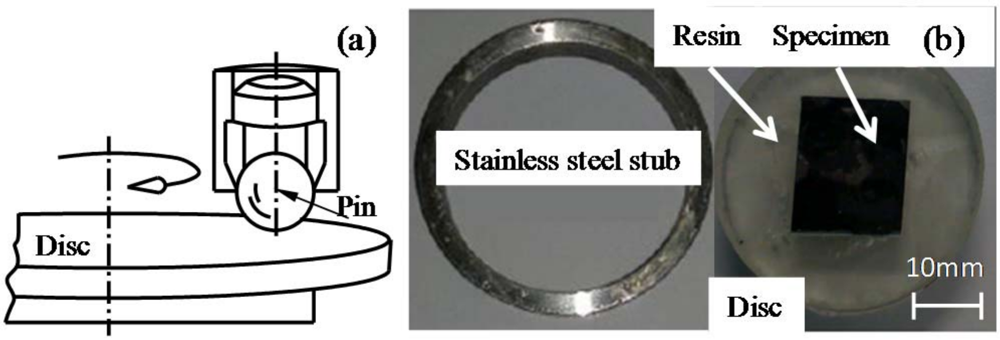

Fig. 3 a) Schematic of the pin-on-disc apparatus and b) photograph of test sample

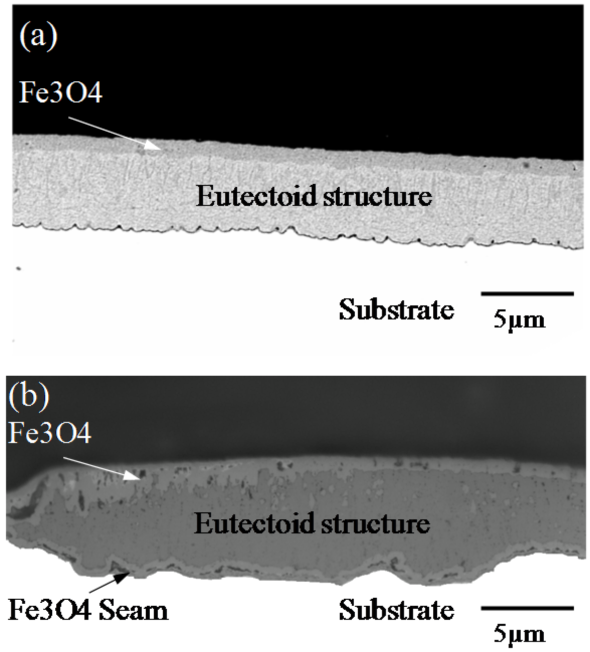

Fig. 4 Oxide scale of low carbon mircroalloyed steel formed at 800°C for 120s then held at 550°C for 60min. a) In dry air b) in 19.5% water vapour contents (vol.%). (Rem: the eutectoid structure consists of α-Fe, Fe_3O_4 and retained FeO).

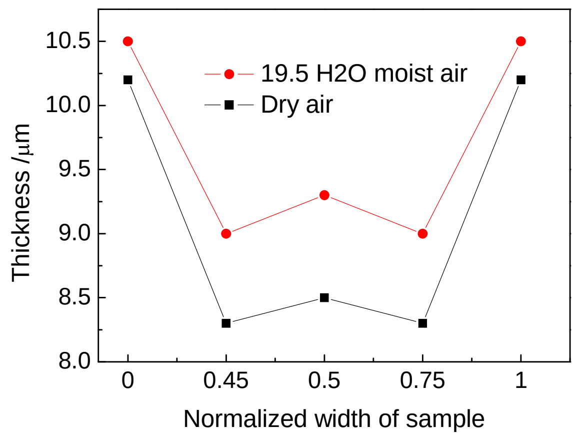

Fig. 5 Thickness of oxide scales formed at 800°C and held at 550°C for 120min in dry air and 19.5% H_2O moisture.

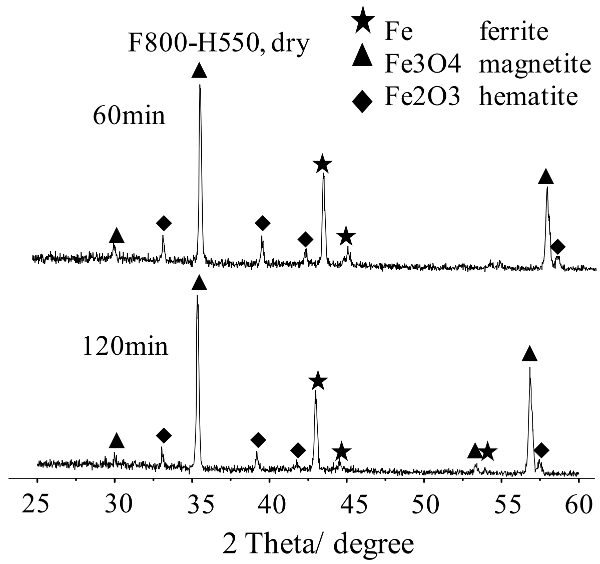

Fig.6 XRD patterns of oxidized surface at 800°C in dry air and held at 550°C for 60 and 120min.

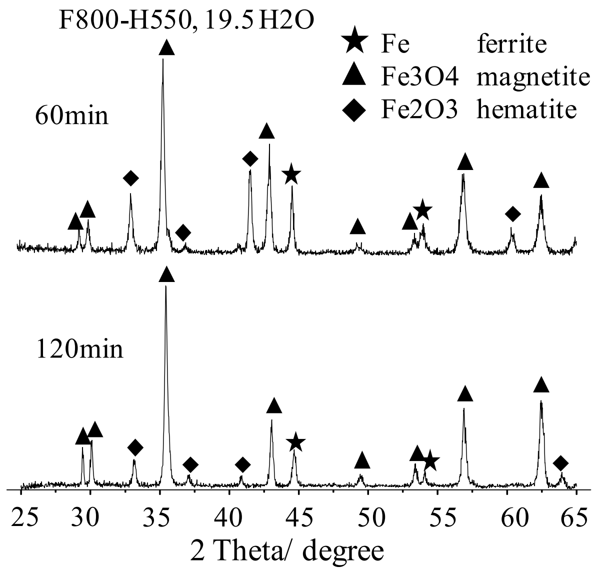

Fig. 7 XRD patterns of oxidized surface at 800°C in 19.5% H_2O moisture and held at 550°C for 60 and 120min.

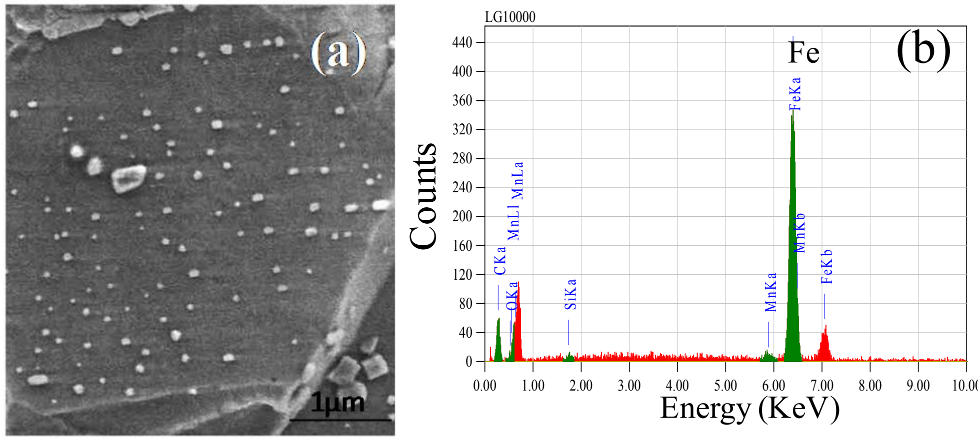

Fig. 8 SEM/EDS analysis of globular precipitation of magnetite particles on wustite surface during isothermal treatments at 550°C for holding 60 min

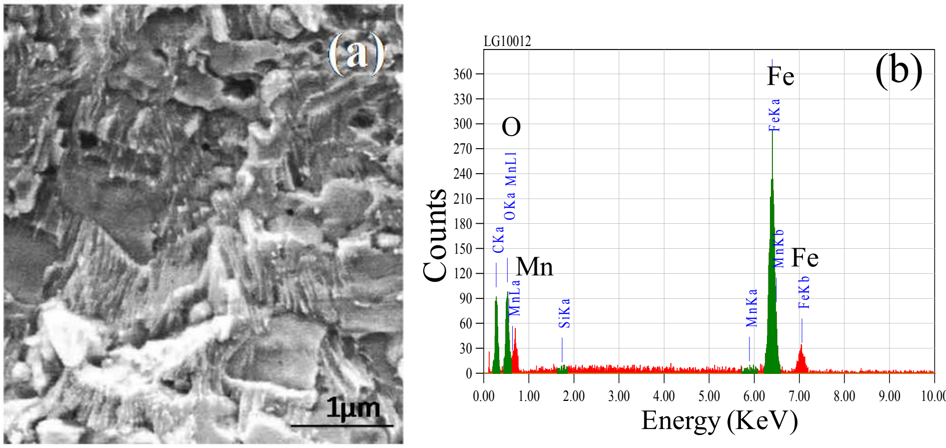

Fig. 9 SEM/EDS analysis of coarse lamellar precipitation of magnetite particles on wustite surface during isothermal treatments at 550°C for holding 120min

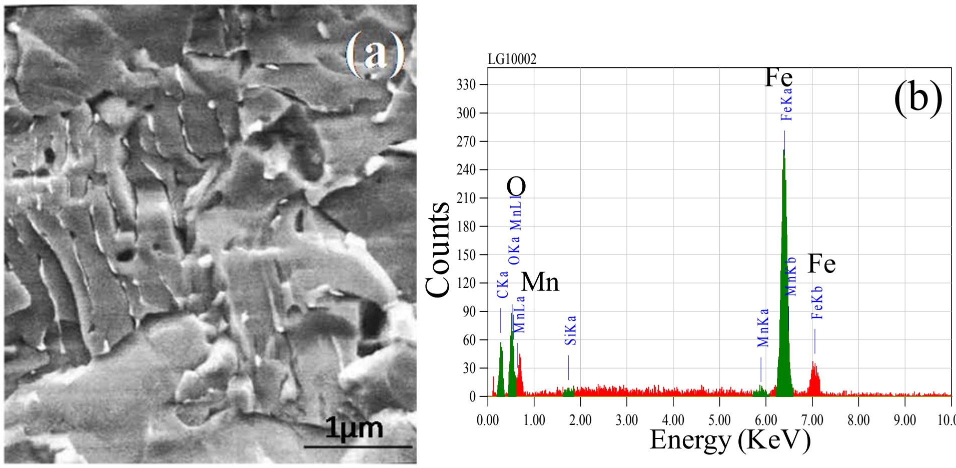

Fig. 10 SEM/EDS analysis of fine lamellar precipitation of magnetite particles on wustite surface during isothermal treatments at 550°C for holding 300min

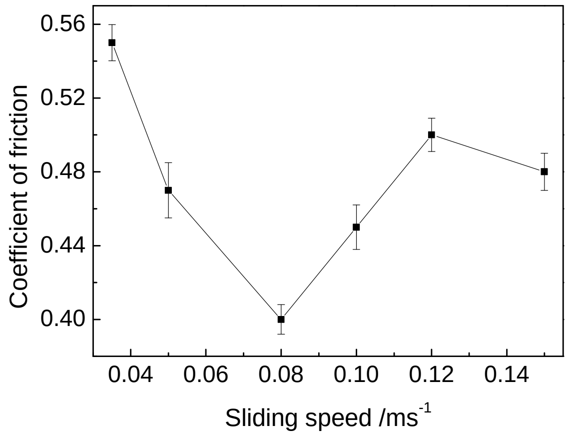

Fig. 11 Effect of sliding speed on coefficient of friction under a normal force of 18N and dry air flow between surfaces

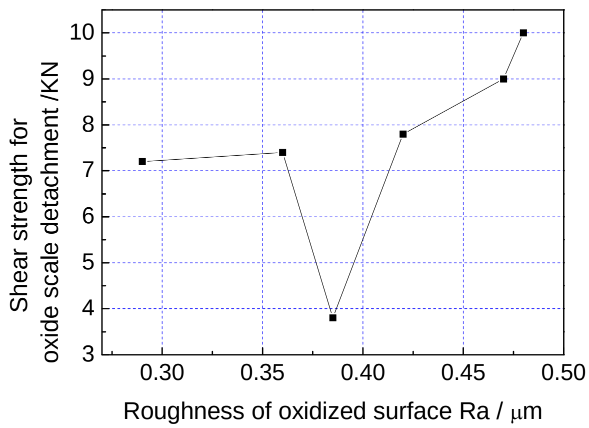

Fig. 12 Correlation between roughness at interface steel/oxide scale and shear strength of oxide scale

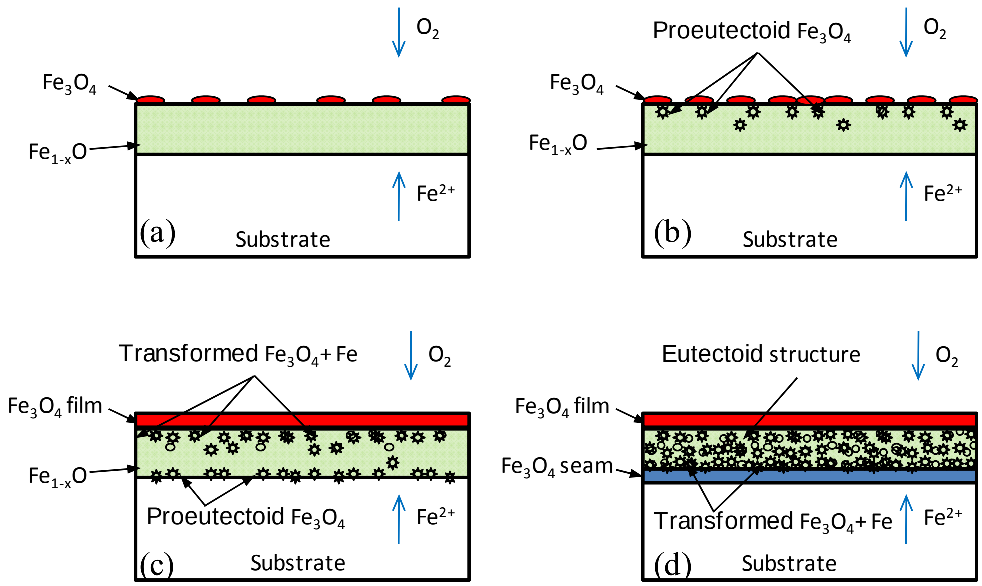

Fig. 13 Schematic illustration of magnetite precipitation from oxide scale during friction tests

Table 1 Mechanical properties for the low carbon mircoalloyed steel

Tensile test: $L_0 = 5.65\sqrt{S_0}$		
Yield strength, MPa	Tensile strength, MPa	Elongation, %
≥ 355	510-610	≥ 24

*L_0, S_0 are the gauge length and the cross-sectional area of working zone for tensile sample, respectively

Table 2 Chemical composition of materials (wt%)

Item	C	Si	Mn	Cr	P	Al	V	Nb	Ti
Steel (disc)	0.1	0.15	1.61	0.21	0.014	0.034	0.041	0.041	0.016
AISI E52100 (pin)	0.98-1.10	0.15-0.30	0.25-0.45	1.30-1.60	0.025				