Crystallographic Texture Based Analysis of $\text{Fe}_3\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$ Scale Formed on a Hot-rolled Microalloyed Steel

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Oxide scale formed on the strip surface during hot rolling has posed a serious obstacle to ensure a defect-free surface of steel products in an ecologically friendly way. Recently, an influential idea is that the tertiary oxide scale with a tailored texture can be expected to enhance surface quality and tribological properties during particular lubrication. In this study, texture evolutions of magnetite (Fe_3O_4) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) in deformed oxide layers formed on a hot-rolled microalloyed steel were investigated by electron back-scattering diffraction (EBSD). Fe_3O_4 develops a strong θ fibre parallel to the oxide growth, and $\alpha\text{-Fe}_2\text{O}_3$ has a dominant $\{0001\}\langle 10\bar{1}0 \rangle$ texture component. This could be explained by surface energy minimisation during oxides growth and transformation between two oxides, which can also be affected by propagation of cracks along high angle grain boundaries in Fe_3O_4 . Our data further demonstrate that a high thickness reduction ($>28\%$) can reduce $\alpha\text{-Fe}_2\text{O}_3$ wedging through Fe_3O_4 cracks, and tailoring Fe_3O_4 texture to $\{111\}$ components can prevent the $\alpha\text{-Fe}_2\text{O}_3$ growth tilting 54.76° from the $\langle 001 \rangle$ crystal direction of Fe_3O_4 . As such, these means can dramatically alleviate disturbance from 'red scale' ($\alpha\text{-Fe}_2\text{O}_3$) during high-temperature steel processing.

KEY WORDS: hot rolling; oxide scale; EBSD; magnetite; hematite; texture.

1. Introduction

Oxidation is one of the most pervasive problems in almost all metals and their alloys processing at elevated temperatures.^{1–4)} Specifically, oxide scale formed in hot strip rolling has posed a serious obstacle, and thereby causes the surface quality of final products to deteriorate.^{5–8)} In most cases, many different surface properties of metals and alloys can dominate surface characteristics of two solids in contact and thereby influence tribological performance.⁹⁾ These surface properties include surface energy, crystallographic orientation, grain boundaries, texturing of surface and crystal structure.^{10,11)} For instance, some results demonstrate that Fe_3O_4 (100) plane is a very rich and complex system, and its surface structure depends critically on surface preparation in the magnetoelectronics field.¹²⁾ It is therefore recently proposed that a tight oxide layer ($\sim 75\%$ magnetite, Fe_3O_4)^{13,14)} with controlled texture, such as Fe_3O_4 (100), can be possible to enhance tribological properties during nanoparticles-additive lubrication, and further improve surface quality of steels.^{9,10)} This is usually associated with the deformation behaviour of oxide scale during hot rolling.^{15,16)} However, characterisation of crystallographic texture evolution in deformed oxide layers has remained elusive.

Microalloyed low carbon steels generally evolve multi-layered oxide scale which consists of two (below 570°C) or three (above 570°C) oxide sub-layers having distinct mechanical properties and growing by different mechanisms.^{2,3)} Correspondingly, wustite (Fe_{1-x}O , with $1-x$ ranging from 0.83 to 0.95) dominates at high temperatures (normally $>650^\circ\text{C}$ for steels), whereas Fe_3O_4 prevails at low temperatures, and hematite (Fe_2O_3) remains low in either case.^{17–19)} The proportion of the three phases within oxide scale at high-temperature oxidation depends greatly on the equilibrium transformation of Fe_{1-x}O or Fe_3O_4 precipitation which is related to heat treatment, atmospheric conditions and alloying elements in the steel.^{20,21)} The growth and microstructure of oxide scale during the continuous cooling from different temperatures and at different cooling rates have been investigated,^{3,22,23)} and it was found that the oxide scale increased in thickness at a lower cooling rate. The microstructural development of oxide scale was observed with Fe_3O_4 precipitates in the Fe_{1-x}O layer at cooling rates of 10 to $60^\circ\text{C}/\text{min}$.³⁾ The Fe_3O_4 and iron eutectoid layer formed near the Fe_3O_4 layer, while a Fe_{1-x}O layer containing Fe_3O_4 precipitates was detected at the inner region when the cooling rate was reduced to $5^\circ\text{C}/\text{min}$.²²⁾ Various explanations for this phase evolution have been proposed, based on an investigation on the isothermal decomposition of the thermally grown Fe_{1-x}O .^{20,21,24)}

Substantial studies on the texture in oxide phases and

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their orientation relationship (OR) is now being investigated via electron backscatter diffraction (EBSD).^{17–19,25–29)} Cubic Fe_3O_4 and Fe_{1-x}O share a strong $\langle 100 \rangle$ texture and a cube-cube OR in undeformed oxide scale whatever the steel substrate.^{17–19)} In contrast, the deformed oxide scale develops a pronounced $\langle 100 \rangle$ fibre component using plane strain compression.^{25,26)} Alternatively, a noticeable microstructure for the precipitation of Fe_3O_4 at either high or low temperature is another product of the Fe_3O_4 layer (called the magnetite seam) formed at the Fe_{1-x}O /steel interface.^{22,30)} Several attempts were made to identify the magnetite seam which was associated with the adherence properties of oxide scale.^{31,32)} In a recent study the orientation of the seam was reported $\{110\}\text{Fe}/\{100\}\text{Fe}_3\text{O}_4$, $\langle 110 \rangle\text{Fe}/\langle 100 \rangle\text{Fe}_3\text{O}_4$ in the case of transforming by continuous cooling from 400°C .³¹⁾ Also, their lattice strain was calculated as 4%. By contrast, the Fe/FeO OR was $\{100\}\text{Fe}/\{110\}\text{FeO}$, $\langle 110 \rangle\text{Fe}/\langle 110 \rangle\text{FeO}$ with a lattice strain of 25%. It is suggested that Fe_3O_4 has better coherency with the steel substrate than Fe_{1-x}O in terms of the conformity of lattice sites of iron oxide with that of the substrate, but these relationships are also limited to the oxide scale thicker than $8\text{ }\mu\text{m}$.³³⁾ For the very thin oxide scale, a Fe/FeO OR was $\{100\}\text{Fe}/\{100\}\text{FeO}$, $\langle 100 \rangle\text{Fe}/\langle 110 \rangle\text{FeO}$ with a lattice strain of 6%.³²⁾ Nevertheless, only limited studies on trigonal $\alpha\text{-Fe}_2\text{O}_3$ indicate its grains grow at an angle of 60° from the $\langle 100 \rangle$ crystal direction of Fe_3O_4 .^{17,18)}

However, ambiguities still remain what kind of texture in deformed Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$ will be developed during hot rolling, and what its evolution will be. Little is also currently known concerning grain boundary characters of cubic Fe_3O_4 and trigonal $\alpha\text{-Fe}_2\text{O}_3$. An attempt will be made in this study to address this deficiency by investigating the texture evolution and grain boundary characters of Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$ in deformed oxide layers after hot rolling-accelerated cooling (HR-AC) tests.

2. Experimental and Analytical Procedures

The material used was a Nb-V-Ti microalloyed low carbon steel in the form of a sheet ($400 \times 100 \times 3\text{ mm}^3$). Its chemical compositions are listed in **Table 1**. These sheets were then ground using SiC papers of 2400 mesh to a surface finish of $0.5\text{ }\mu\text{m}$, and cleaned in a solution of acetone. HR-AC experiments were immediately performed on a 2-high Hille 100 experimental mill with 225 mm diameter rolls, combined with a newly developed accelerated cooling system. Full details of the experimental instruments can be found elsewhere.^{15,34)} The following procedure was carried out for every HR-AC test. Each sample was reheated to 900°C at a rate of 1.7°C/s under a high purity inert gas atmosphere, and held for 15 min to ensure a uniform temperature and homogenise the austenite grains. The reheated sample was then given a single rolling thickness reduction (TR, 10%–28%) at a rolling speed of 0.3 m/s without any lubrication followed by an accelerated cooling with the

cooling rates (CRs) of $10\text{--}28^\circ\text{C/s}$. Finally, the HR-AC samples were air cooling to obtain the tertiary oxide scale at room temperature. This presumes, of course, the grown oxide layers are subject to the same deformation ratios as the corresponding hot-rolled steel substrate.

Sample preparation of oxide scale using conventional polishing techniques is more complicated and time-consuming than that of a single-phase matrix because the oxide phases and the steel substrate need to polish at different rates.^{35,36)} In this study, a Leica EM triple ion beam cutter (TIC020) system was used for precise processing of oxidised samples for subsequent examination with electron microscopes. Samples were cut from the centre of the hot-rolled sheet along the plane of the rolling direction (RD) and normal direction (ND). After gold deposition, the edges for cross sectional analysis were ground by SiC papers with 2000 mesh, and then ion-milled at 6 kV for 5 h using a TIC020 system. Microstructure characterisation was studied using a JEOL JSM 7001F Schottky field emission gun (FEG) scanning electron microscope (SEM) with a Nordlys-II (S) EBSD detector, operated at an acceleration voltage of 15 kV, a probe current of around 2–5 nA, a working distance of 15 mm, and a step size of $0.125\text{ }\mu\text{m}$.

Post-processing of acquired dataset was carried out using Channel 5 software, where both texture and misorientation data were extracted from the EBSD maps. First for orientation noise reduction, an angular resolution for the grain reconstruction was maintained at a constant value of 2° . Consequently, $2^\circ \leq \theta < 15^\circ$ misorientations are defined as low-angle grain boundaries (LAGBs), whereas, the high-angle grain boundaries (HAGBs) are $\theta \geq 15^\circ$. Secondly, phase identification is based on the structural data related to the crystal symmetry and lattice parameters of the suspected phases. In case of the oxide scale, each phase has a different space group ($\alpha\text{-Fe}$, $Im\bar{3}m$; Fe_{1-x}O , $Fm\bar{3}m$; Fe_3O_4 , $Fd\bar{3}m$; $\alpha\text{-Fe}_2\text{O}_3$, $R\bar{3}c$), and different lattice parameters. $\alpha\text{-Fe}$, Fe_{1-x}O and Fe_3O_4 in cubic symmetry with lattice parameters (a) of 0.287 nm, 0.431 nm, and 0.840 nm respectively, and $\alpha\text{-Fe}_2\text{O}_3$ in a trigonal structure with $a = 0.504\text{ nm}$ and $b = 1.377\text{ nm}$.^{17,25,29)} The EBSD phase maps were finally divided into three subsets comprising $\alpha\text{-Fe}$, Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$ for texture based analysis. Orientation distributions of the three subsets were calculated from the data on individual grain orientations collected. The grain orientation $g = (\phi_1, \Phi, \phi_2)$ is expressed by the three Euler angles in Bunge notation.^{36,37)} $\alpha\text{-Fe}$ and Fe_3O_4 have a cubic structure and their orientation distribution function (ODF) sections are depicted using the $\phi_2 = 0^\circ$ and 45° , for trigonal $\alpha\text{-Fe}_2\text{O}_3$ the ODF sections with $\phi_2 = 0^\circ$ and 30° are used, in contrast.³⁶⁾ ODF sections were calculated using the discrete binning method with a bin size of 5° and Gaussian smoothing.

3. Results

3.1. Microstructure Characterisation

The microstructure of the as-received steel substrate was

Table 1. Chemical compositions of the microalloyed low carbon steel.

Elements	C	Si	Mn	P	Cr	S	Al	N	Nb + V + Ti	Fe
wt. %	0.1	0.15	1.61	0.014	0.21	0.002	0.034	0.003	0.016–0.041	Bal.

analysed prior to HR-AC experiments. **Figure 1** shows a typical SEM image of the etched microalloyed steel using 2% nital solution for 20 s. The microstructure of steel substrate consists of 94% fine-grained polygonal α -Fe and 6% pearlite. The grain size of polygonal α -Fe was determined as 3 μm by using circular intercept method according to ASTM: E112-10. As such, the steel substrate in EBSD based analysis is confined to single α -Fe phase due to only a small amount of pearlite in this material.

EBSD phase maps in **Fig. 2** indicate the distribution of oxide phases formed on the steel substrate subjected to different TRs and CRs. The oxide scale consists of a two-layered microstructure with a thin outer layer of α -Fe₂O₃ and an inner duplex Fe₃O₄ layer. The retained Fe_{1-x}O and eutectoid α -Fe disperse over the Fe₃O₄ matrix. α -Fe₂O₃ near the surface gradually penetrates into the cracks within the oxide scale shown in Figs. 2(a) and 2(b). Its distribution in the Fe₃O₄ matrix reduces dramatically with the decrease of

Fig. 1. Surface morphology of the as-received microalloyed steel substrate.

pores or cracks when the TR is high (28% in Fig. 2(c)). It is inferred that an increase of TR can suppress the transformation of Fe₃O₄ to α -Fe₂O₃ in the oxide layers after HR-AC process. This is due partly to a refining of Fe₃O₄ grain size (2–3 μm) at a high TR of 28% (Fig. 2(c)). A large amount of fine granular Fe₃O₄ grains with relatively dense arrangement can alleviate transformation of Fe₃O₄ to α -Fe₂O₃ by oxidation of Fe²⁺ to Fe³⁺.

3.2. Grain Boundary Characters of Fe₃O₄/ α -Fe₂O₃

The EBSD boundary maps in **Fig. 3** illustrate a gradual and uniform collapse of the columnar boundary structure. The relatively high TR and CR of 28%, 28°C/s produced large amount of granular Fe₃O₄ grains (2–3 μm in size). Indeed, the grain-refined Fe₃O₄ could be affected by Fe_{1-x}O decomposition of hot-rolled samples cooling from high temperature.^{20,21,24,38} When the similar TRs of 10%, there are much more LAGBs occurred at the low CR of 10°C/s in Fig. 3(a). With the low TR of 13%, Fe₃O₄ contains very few LAGBs at the CR of 23°C/s (Fig. 3(b)), whereas most of LAGBs were found in the sample with the high TR (Fig. 3(c)). This suggests that a low CR and high TR could enhance the presence of LAGBs. These LAGBs are generally believed to suppress the propagation of cracking during hot rolling. It is further inferred that the coupled effect of TR and CR could be imposed on Fe_{1-x}O decomposition into Fe₃O₄ below the eutectoid point of 570°C.^{20,21}

To further quantify the HAGBs between emerging α -Fe₂O₃ and Fe₃O₄, **Fig. 4** provides the distributions of misorientation axes/angle ($\geq 15^\circ$) of the sample after a TR of 10% and CR of 10°C/s. The distribution of misorientations axes for Fe₃O₄ in angle ranges has been processed to give a high proportion of coincident site lattice (CSL) boundaries.

Fig. 2. EBSD phase maps for α -Fe, Fe_{1-x}O, Fe₃O₄ and α -Fe₂O₃ of the samples with the TRs and CRs of (a) 10%, 10°C/s, (b) 13%, 23°C/s and (c) 28%, 28°C/s.

Fig. 3. EBSD grain boundary maps of the samples after HR-AC tests at the TRs and CRs of (a) 10%, 10°C/s, (b) 13%, 23°C/s and (c) 28%, 28°C/s. Grey = LAGBs, black = HAGBs.

Fig. 4. Distributions of misorientation axes for (a) Fe_3O_4 , (b) $\alpha\text{-Fe}_2\text{O}_3$, of the sample with a TR of 10% and a CR of 10°C/s, and (c) corresponding distribution of misorientation angles ($\geq 15^\circ$).

The peaks in the $57\text{--}63^\circ$ section (Fig. 4(a)) correspond to $60^\circ/\langle 111 \rangle$ ($\Sigma 3$) misorientation marked in Fig. 4(c). Misorientation peaks occur in $\alpha\text{-Fe}_2\text{O}_3$ (Fig. 4(b)) for axes near $\langle 0001 \rangle$ in the angle range of $27\text{--}63^\circ$, and $\langle 1\bar{1}02 \rangle$ in the angle range of $63\text{--}83^\circ$. The distribution of misorientation angles (Fig. 4(c)) in cubic crystals has a maximum at 45° and a cutoff at 62.8° , whereas trigonal $\alpha\text{-Fe}_2\text{O}_3$ has a max-

imum at 60° and a cutoff at 95° . For $\alpha\text{-Fe}_2\text{O}_3$ the relatively high densities correspond to $57.42^\circ/\langle 1210 \rangle$ ($\Sigma 13b$) and $84.78^\circ/\langle 0\bar{1}10 \rangle$ ($\Sigma 19c$).³⁹ In any case, these grain boundary characters in Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$ can provide deep insight for the penetration of $\alpha\text{-Fe}_2\text{O}_3$ into Fe_3O_4 scale during air cooling after hot rolling.

3.3. Texture Development of $\text{Fe}_3\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$

A typical quantitative evaluation was conducted to obtain the texture evolution in $\text{Fe}_3\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$ scale at the different TRs and CRs. The representation of pole figures (PF) for $\text{Fe}_3\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$ scale at a TR of 13% and a CR of 23°C/s has been given in Fig. 5. Fe_3O_4 develops the strong $\{100\}$ and $\{110\}$ fibres and a relatively weak $\{111\}$ texture component (Fig. 5(a)). The $\{0001\}$ basal planes of $\alpha\text{-Fe}_2\text{O}_3$ are approximately parallel to the interface with Fe_3O_4 , thus building

the fibre axis along the surface normal direction (Fig. 5(b)). The $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$ prismatic planes lie nearly perpendicular to the magnetite surface. The results are slightly different from the previous investigation where the $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$ fibres texture develop instead.³⁹⁾ This could be due to the oxide scale without deformation in previous studies.³⁹⁾

Figure 6 shows texture development of Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$ in deformed oxide layers and their intensity distributions along associated fibres or texture components. Fe_3O_4

Fig. 5. $\{100\}$ and $\{111\}$ pole figures (PF) for (a) Fe_3O_4 and (b) $\{0001\}$, $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ PF for $\alpha\text{-Fe}_2\text{O}_3$ at a TR of 13% and a CR of 23°C/s .

Fig. 6. Development of texture intensity $f(g)$ along the (a) θ fibre of Fe_3O_4 , (c) $\langle 1010 \rangle$ fibre of $\alpha\text{-Fe}_2\text{O}_3$, of the samples with different TRs and CRs, and ODF sections for (b) Fe_3O_4 and (d) $\alpha\text{-Fe}_2\text{O}_3$ at a TR of 28% and a CR of 28°C/s .

has a cubic structure and its ODF sections are depicted using the $\phi_2 = 0^\circ$ and 45° (Fig. 6(b)) in terms of the Bunge system.³⁷⁾ In contrast, for trigonal $\alpha\text{-Fe}_2\text{O}_3$ the ODF sections with $\phi_2 = 0^\circ$ and 30° (Fig. 6(d)) are used.³⁶⁾ θ fibre develops in Fe_3O_4 superimpose on $\phi_2 = 0^\circ$ section at $\phi = 0^\circ$ with the rotations of $\langle 100 \rangle // \text{ND}$.^{17,19,25,29)} Figure 6(a) shows the intensity distribution of the θ fibre in Fe_3O_4 on the samples subjected to various deformation conditions. $\langle 10\bar{1}0 \rangle$ fibre component in $\alpha\text{-Fe}_2\text{O}_3$ (Fig. 6(c)) lies on $\phi_2 = 30^\circ$ section and corresponds to orientations along $\Phi = 90^\circ$.

As seen in Fig. 6(b), Fe_3O_4 in deformed oxide layers holds a strong θ fibre parallel to the oxide growth, where pronounced orientations develop between $\{001\}\langle 100 \rangle$ cube and $\{001\}\langle 110 \rangle$ rotated cube components. With the increase of TRs and CRs (Fig. 6(a)), the cube orientations slightly shift toward the $\langle 210 \rangle$ direction, and finally lead to a relatively strong $\{100\}\langle 210 \rangle$ component with the intensity of $f(g) = 6.7$. θ fibre is also found in the undeformed Fe_3O_4 left at 650 and 950°C after reheating at 1050°C.^{25,26)} Thus, the presence of $\{100\}\langle 001 \rangle$ cube and $\{001\}\langle 110 \rangle$ rotated cube components can be attributed to grain growth during high temperature oxidation. Nevertheless, the $\{100\}\langle 210 \rangle$ texture can dominate during subsequent deformation by external force. Moreover, it cannot be seen any texture components along $\{111\}$ slip planes occurred in the most face-centred cubic (fcc) materials.

Compared to the cubic Fe_3O_4 , the trigonal $\alpha\text{-Fe}_2\text{O}_3$ in deformed oxide layers has similar texture components with the nearly same strength under various deformation conditions. The pronounced orientations of $\alpha\text{-Fe}_2\text{O}_3$ (Fig. 6(d)) comprise a fibre running along $\{0001\}$ basal plane which includes a dominant $\{0001\}\langle 10\bar{1}0 \rangle$ and relatively weak $\{0001\}\langle 2\bar{1}\bar{1}0 \rangle$ texture components. Particularly, the maximum texture intensity lies on the $\{0001\}\langle 10\bar{1}0 \rangle$ orientation ($f(g) = 14.4$ in Fig. 6(c)) of the sample at a higher TR of 28% and CR of 28°C/s. The $\{0001\}$ basal plane of $\alpha\text{-Fe}_2\text{O}_3$ is crystallographic plane having close-packed oxygen anions, thus oxide growth and deformation tend to occur across close-packed oxygen planes.^{17,40)} Nonetheless, $\alpha\text{-Fe}_2\text{O}_3$ in a trigonal structure generally has independent slip systems, namely $\{0001\}\langle 2\bar{1}\bar{1}0 \rangle$, $\{1\bar{2}10\}\langle 10\bar{1}0 \rangle$, $\{1\bar{2}10\}\langle 10\bar{1}\bar{1} \rangle$, $\{1\bar{1}02\}\langle 01\bar{1}\bar{1} \rangle$, and $\{10\bar{1}0\}\langle 01\bar{1}\bar{1} \rangle$.^{36,39,41)} In this case, the rolling texture development of $\alpha\text{-Fe}_2\text{O}_3$ may attribute to the effect oxygen content through changes of the critical resolved shear stress of the various slip systems.^{36,41)}

4. Discussion

The results presents here demonstrate that Fe_3O_4 develops a strong θ fibre parallel to the oxide growth, and $\alpha\text{-Fe}_2\text{O}_3$ carries a fibre running along $\{0001\}$ basal plane. This finding that texture evolution of Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$ positively related to TRs is similar to those two previous studies.^{25,26)} Here it is possible to find out the cause of what is happening. The driving energy for the sharp texture formation observed in Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$ can attribute to surface energy minimisation when the steels suffering high temperature oxidation during hot rolling. For cubic Fe_3O_4 with a spinel structure, the surface energy increases in order of $\{100\}$ (1.5 J m^{-2}), $\{110\}$ (1.8 J m^{-2}) and $\{111\}$ (2.2 J m^{-2}).^{17,18)} Hence, this results in the main θ fibre running through $\{001\}\langle 100 \rangle$

cube and $\{001\}\langle 110 \rangle$ rotated cube components (Fig. 6). Indeed, previous results also reveal that the $\{001\}$ planes of Fe_3O_4 depends critically on sample preparation and heat treatment.^{10,42)} In case of $\alpha\text{-Fe}_2\text{O}_3$ with a strong preferential crystallographic orientation in the normal direction of the $\{0001\}$ basal plane, the texture strength is thought to be driven by the low surface energy (1.52 J m^{-2}) of the $\{0001\}$ plane of $\alpha\text{-Fe}_2\text{O}_3$.⁴¹⁾ The rolling texture of $\alpha\text{-Fe}_2\text{O}_3$ has a strong $\{0001\}\langle 10\bar{1}0 \rangle$ component (Fig. 6) which is a direct consequence of the favoured basal plane slip.

Transformation of Fe_3O_4 to $\alpha\text{-Fe}_2\text{O}_3$ by oxidation of Fe^{2+} to Fe^{3+} can be another closely related process responsible for the observed texture evolution in deformed oxide layers. Fe^{2+} ions oxidised to Fe^{3+} during high-temperature short-time processing, such as the tertiary oxide scale,^{3,11,13)} are dependent primarily on crystallographic similarities of Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$. $\{111\}$ planes of Fe_3O_4 and $\{0001\}$ planes of $\alpha\text{-Fe}_2\text{O}_3$ are both parallel and perpendicular to the three-fold axes. For a fcc crystal interfaced to a trigonal close packed (hcp) crystal, the preferred orientation relationships are given by $(111)_{\text{fcc}} // (0001)_{\text{hcp}}$ and $(\bar{1}10)_{\text{fcc}} // (10\bar{1}0)_{\text{hcp}}$, where the close-packed planes and directions are matched across the interface.^{40,41)} Given that the formed Fe_3O_4 after thermodynamically unstable Fe_{1-x}O has $\langle 001 \rangle$ fibre texture (Fig. 6), and also the interplanar angle between $\{111\}$ and $\{001\}$ planes is 54.76° in cubic structure, $\alpha\text{-Fe}_2\text{O}_3$ grains must grow at an angle of 54.76° from the $\langle 001 \rangle$ crystal direction of Fe_3O_4 . Thus, Fe^{2+} ions resulting from diffusion at Fe_3O_4 boundaries react with oxygen and oxidise as thin platelets of $\alpha\text{-Fe}_2\text{O}_3$ with c -axes perpendicular to the oxide growth and the a -axes in the plane of oxide growth ($\{0001\}\langle 10\bar{1}0 \rangle$ texture component). These results confirm that if $\alpha\text{-Fe}_2\text{O}_3$ grows on a $\{100\}$ Fe_3O_4 , its grains will be tilted at an angle of 54.76° to the Fe_3O_4 matrix, whereas for a $\{111\}$ Fe_3O_4 , the epitaxial growth of $\alpha\text{-Fe}_2\text{O}_3$ $\{0001\}$ will occur. Similar result has been recently reported for other single crystal oxide scales.⁴¹⁾

In addition to the texture developed in undeformed oxide scale, the variation of crystallographic planes is dominant in Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$ as the different ORs of steel substrate.^{17,19,29)} For most polycrystalline substrates, a noticeable feature in Fe_3O_4 is the evolution of crystallographic direction, whereas the texture evolution of $\alpha\text{-Fe}_2\text{O}_3$ varies in the crystallographic planes.^{17,29)} This is a direct consequence of the minimisation of surface energy and lattice strains from their mismatch. In case of Fe_3O_4 , the strong textures generally develop on the planes of $\{100\}$ whatever in undeformed or deformed oxide scale.^{25,29)} The difference is that the deformed Fe_3O_4 holds the texture development shifting from the $\langle 100 \rangle$, $\langle 110 \rangle$ to $\langle 210 \rangle$ directions in Figs. 5(a) and 6(b). Nevertheless, $\alpha\text{-Fe}_2\text{O}_3$ is totally another story before and after deformation of oxide scale. The undeformed $\alpha\text{-Fe}_2\text{O}_3$ formed at low-temperature oxidation has the $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$ fibre textures,^{29,41)} whereas the rolling texture of $\alpha\text{-Fe}_2\text{O}_3$ has a strong $\{0001\}\langle 10\bar{1}0 \rangle$ component (Fig. 5). This infers that the favoured basal plane slip dominates the deformed $\alpha\text{-Fe}_2\text{O}_3$ compared to the undeformed oxide scale.

Lastly, the formation and propagation of cracks along the Fe_3O_4 grain boundaries create paths for easy air penetration, and therewith allow further oxidation (Fig. 2(a)). It is believed that low-angle and low- Σ CSL boundaries in micro-

structure offer obstacles to the propagation of cracks, as they minimise the solute effects and reduce the interaction between the interfaces and glissile dislocation.⁴³⁾ In this case, the oxide scale is easy to crack in presence of $\Sigma 13b$ and $\Sigma 19c$ in $\alpha\text{-Fe}_2\text{O}_3$ compared to Fe_3O_4 with $\Sigma 3$ (Fig. 4(c)). Therefore, two means can be considered for the decrease and further easy removal of $\alpha\text{-Fe}_2\text{O}_3$. One is that a desired TR (>28%) can reduce cracks along the Fe_3O_4 grain boundaries and thereby prevent further oxidation to $\alpha\text{-Fe}_2\text{O}_3$. Alternatively, tailoring the texture of initial Fe_3O_4 to $\{111\}$ components using particular lubrication can avoid $\alpha\text{-Fe}_2\text{O}_3$ growth titling 54.76° to the (100) Fe_3O_4 matrix. This is practically important to dramatically alleviate disturbance from 'red scale' ($\alpha\text{-Fe}_2\text{O}_3$) during hot rolling, when Fe_3O_4 is oxidised to red powdery $\alpha\text{-Fe}_2\text{O}_3$ during air cooling.^{6,8)}

5. Conclusions

In this study microstructure and texture evolution of $\text{Fe}_3\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$ scale form on a Nb-V-Ti steel subjected to the TRs of 10%–28% and CRs of 10–28°C/s were systematically analysed. The following conclusions can be drawn.

(1) The oxide scale consists of a thin $\alpha\text{-Fe}_2\text{O}_3$ outer layer and an inner duplex Fe_3O_4 layer. Grain refinement of Fe_3O_4 (2–3 μm) at a TR of 28% can suppress the penetration of $\alpha\text{-Fe}_2\text{O}_3$ into the oxide scale.

(2) The oxide scale comprises a high proportion of LAGBs at low CR and high TR. These LAGBs are generally believed to suppress the propagation of cracking during hot rolling. For CSL boundaries, Fe_3O_4 on the samples at a TR of 10% and CR of 10°C/s develops $60^\circ/\langle 111 \rangle$ ($\Sigma 3$), and $\alpha\text{-Fe}_2\text{O}_3$ for $57.42^\circ/\langle 1\bar{2}10 \rangle$ ($\Sigma 13b$) and $84.78^\circ/\langle 0\bar{1}10 \rangle$ ($\Sigma 19c$).

(3) Fe_3O_4 carries strong θ fibre parallel to the oxide growth, which includes $\{100\}\langle 001 \rangle$ and $\{001\}\langle 110 \rangle$ texture components, because of surface energy minimisation on $\{100\}$ planes of Fe_3O_4 . $\alpha\text{-Fe}_2\text{O}_3$ develops $\{0001\}\langle 10\bar{1}0 \rangle$ component as the favoured basal plane slip. The $\alpha\text{-Fe}_2\text{O}_3$ growth on θ fibre Fe_3O_4 is 54.76° tilted from the $\langle 001 \rangle$ crystal direction of Fe_3O_4 .

(4) Two means are proposed for easy removal of $\alpha\text{-Fe}_2\text{O}_3$. One is that LAGBs can act as obstacles to cracks propagation further to prevent $\alpha\text{-Fe}_2\text{O}_3$ penetration. Another, Fe_3O_4 with $\{111\}$ texture components can be used to form uniform $\alpha\text{-Fe}_2\text{O}_3$. The understanding we have gained as to how texture and grain boundary take place could aid in the choice and design of desired oxide scale available through high-temperature steel processing.

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