

EFFECTS OF TITANIUM AND NIOBIUM ON MICROSTRUCTURE AND MECHANICAL ADHESION OF THERMAL OXIDE SCALES ON HOT-ROLLED LOW CARBON STEEL

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Abstract

Improvement in strengthening steel without losing its ductility is the main development in the steel industry. The presence of a small amount of Ti and Nb concentrations significantly increases the strength of hot-rolled low carbon steel. In order to attain the finishing temperature of the hot-rolling process, the alloys are processed under 900°C in 17.2% steam mixed with an oxygen atmosphere and pure oxygen atmosphere for 1 min and 5 mins, respectively. The small amount of Ti/Nb additions influences the grain size and scale adhesion. The grain size was reduced by 16% in the Ti/Nb addition sample resulting in better strength properties by means of grain refinement. The Ti/Nb addition sample is less sensitive to the water vapour content than the base metal in an oxidizing atmosphere. The oxide scale in the Ti/Nb sample was found to have a Ti-doped magnetite phase. In both oxidizing atmospheres, the Ti/Nb addition sample showed lower strain initiating at the first spallation than that of the base metal sample, resulting in a weaker oxide scale adhesion.

Keywords: Ti addition, Nb addition, microalloyed steel, thermal oxide scale

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Introduction

Demands for the production of plate or strip products for hot-rolling and cold-rolling processes are increasing due to the growth of the automotive industries and structural part applications. The challenge of the ongoing trend is a conventional hot strip product which is developed to have better mechanical properties by the addition of alloying elements. In parallel, the high level of productivity and surface quality of the cold-rolled product must be maintained (Chandra-ambhorn *et al.*, 2013). For instance, the strips need a good surface quality without leaving oxide scale on the surface prior to being subjected to the cold-rolling process (Chen and Yeun, 2003).

In fact, there is an oxidizing atmosphere in the conventional hot-rolling process at elevated temperatures, which is 1 reason why the oxide scale forms on the slab during reheating (Chen and Yeun, 2003). The influence of scale removability may be affected by the microstructure of the oxide scale on an interface and adhesion between the scale and metal substrate. A thick layer of oxide scale consists of 3 different layers known as the primary, secondary, and tertiary structures (Ginzburg, 1989). The oxide scale of steel consists of an outer very thin hematite surface layer (Fe_2O_3), a thin magnetite layer (Fe_3O_4), and a thick inner wüstite layer (FeO) (Hussey *et al.*, 1977; Chen and Yeun, 2001; Chen and Yeun, 2005; Nilsonthi *et al.*, 2017). The microstructure of oxide scale affects the descaling process due to an adhesion of the oxide scale-steel substrate interface.

In recent years, the high strength of microalloyed steels has been substituted for the hot-rolled low carbon strip with a similar strength yet without addition of the heat treatment process (Li *et al.*, 2016). The strength of the microalloyed steels originates from a combination of grain refinement and precipitation strengthening by using a microalloying element such as niobium, titanium, or a combination of both. A modern research study of the oxide scales' characterization on microalloyed steel by Liu *et al.* (2013) demonstrated the thickness fraction of the oxide scale layers between

microalloyed steel and pure iron steel. They found that when increasing the oxidizing temperature from 900 to 1,200°C in an argon atmosphere, the thickness fraction of the wüstite layer in the microalloyed steel increases and that of the magnetite layer decreases. The thickness ratio of the hematite, magnetite, and wüstite layers reaches a constant ratio (1:9:90) when the temperature is higher than 1,100°C. The influence of the alloying elements is the main reason for the difference in the thickness ratio between the microalloyed steels and low-carbon steels.

However, it is undeniable that there is an influence of the water vapour in the hot-rolling process used as a water coolant for removing the oxide scale and reducing the strip temperature, resulting in increasing humidity in the atmosphere. A study by Chandra-ambhorn *et al.* (2013) found that the humidified atmosphere was detrimental to the scale adherence on low carbon steel in dry oxygen and oxygen containing 20% of water vapour atmosphere at 815°C during a period up to 30s. Rahmel (1965) and Chandra-ambhorn and Klubvihok (2016) showed that there was an accumulation of pores or vacancies at the iron/ wüstite interface in the presence of water vapour for an oxidation time longer than 1 h. Contrastingly, a study by Chen and Yeun (2013) showed a different result. Scale was found to have a good, compact adherence in low carbon and silicon steel under an oxidizing atmosphere of 17.2% and 24.8% water vapour content at 1,098°C. This is crucial to understanding the microstructure of oxide scale layers, scale adhesion, and oxidation rates in various conditions and investigating the influence of water vapour in the conventional hot-rolling process.

Nevertheless, there are few studies regarding the effect of the oxidizing atmosphere on microalloyed (Ti/Nb) steel. Therefore, the purpose of this study is to understand the effect of the Ti/Nb alloying elements on the microstructure and mechanical adhesion of the oxide scale on hot-rolled low carbon steel in 2 different atmospheres, which are the humidified (17.2%

water vapour with oxygen) and pure oxygen atmospheres.

Materials and Methods

Hot-rolled low carbon steel, as the base metal (BM) samples, and Ti/Nb addition microalloyed steel samples were provided by Sahaviriya Steel Industries PLC. The samples were cut into a dogbone shape according to ASTM E8M with a total length of 100 mm, as shown in Figure 1. The chemical compositions of the BM and Ti/Nb addition samples are shown in Table 1. Standard metallographic techniques, wet polishing with sandpapers and cloth polishing with colloidal alumina suspension, were used for optical microscope (OM) and scanning electron microscope (SEM) sample preparation. The hot-rolled samples were subjected to heat treatment at 900°C for 1 min and 5 min in the following conditions; a humidified atmosphere (17.2% water vapour with oxygen) and pure oxygen atmosphere.

The observation of the oxide scale microstructure was performed using an OM Nikon Eclipse MA20 (Nikon Corporation, Tokyo, Japan) and SEM JEOL JSM-5410LV (JEOL Ltd., Tokyo, Japan). The ImageJ software was used to measure the thickness of the oxide scale. The x-ray diffraction (XRD) technique, carried out with a JDX-8030 model (JEOL Ltd.) using Cu K α radiation, was

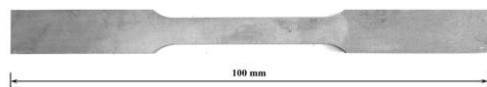


Figure 1. Sample in a dogbone shape with a total length of 100 mm, according to ASTM E8M standard

performed for the oxide phase analysis. A standard XRD database was obtained from AtomWork produced by the National Institute for Materials Science (NIMS) and the ICSD reference number by FIZ Karlsruhe.

The mechanical adhesion of the oxide scale of all conditions was performed using a tensile test. A maximum load of 50 kg force was used with a strain rate of 0.07 s⁻¹. Two crossheads were subjected at the grip section of the tensile specimen. The tensile machine was equipped with an optical lens, which was applied for monitoring the evolution of scale failure and it captured the scale surface spallation during straining. A minimum of samples for each condition 3 was subjected to a given imposed strain with ex-situ imaging of the scale surface after straining in the tensile machine. The strain initiating at the first spallation (% ϵ_{sp}) presents the strength of scale adhesion (Chandra-ambhorn and Klubvihak, 2016) and the spallation ratio is an area fraction of the oxide scale that spalled out per the total probe area (Nilsonthi *et al.*, 2017)

Results and Discussion

Mass Gain as a Function of Time and Oxide Scale Thickness

Figure 2 illustrates a mass gain of the BM and Ti/Nb addition samples as a function of the oxidation time. Table 2 summarizes the oxidation rate by mass gain per unit area (mg/cm²) and overall oxide scale thickness (μ m) in both samples.

In the humidified atmosphere, the mass gain of the BM sample is 3.62 mg/cm² at 1 min and it further increases to 6.51 mg/cm² after 5 mins' oxidation time, corresponding to the thickness of the oxide scale of 28.67 μ m and 32.53 μ m, respectively. Also, the oxidation

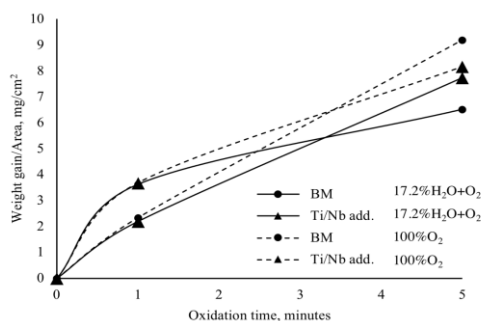
Table 1. The chemical compositions of the base metal and Ti/Nb addition samples

	Chemical composition (wt.%)						
	Fe	C	Mn	Si	Cu	Ni	Cr
BM	Bal.	0.15	1.02	0.02	0.03	0.02	-
Ti/Nb add.	Bal.	0.08	1.5	0.02	0.02	0.01	0.02

Ti+Nb
0.05-0.08 (max.)

Table 2. The mass gain value corresponding to total oxide scale in each condition

Samples	Oxidation time (min)	Mass gain (mg/cm ²)	oxide scale (μm)
Humidified atmosphere			
Base metal	1	3.62	28.67
	5	6.51	32.53
Ti/Nb addition	1	2.19	69.42
	5	7.73	71.81
Pure Oxygen atmosphere			
Base Metal	1	2.34	26.49
	5	9.19	21.11
Ti/Nb addition	1	3.68	71.65
	5	8.16	70

**Figure 2. Mass gain versus oxidation time for 1 min and 5 min in the base metal and Ti/Nb addition samples**

rate of the Ti/Nb addition sample is slightly lower than that of the BM sample at the initial oxidation stage (1 min), which is 2.19 mg/cm², and later increases to 7.73 mg/cm² after 5 min oxidation time, corresponding to the thickness of the oxide scale of 69.42 μm and 71.81 μm, respectively. It is worth noting that the oxide scale of the Ti/Nb addition sample formed more thickly than that of the BM sample since the mass gain of the Ti/Nb addition after 5 min was substantially higher than that of the BM sample.

On the other hand, in a pure oxygen atmosphere, the Ti/Nb addition sample had a higher mass gain, which was 3.68 mg/cm² and a further increase to 8.16 mg/cm², than that of the BM sample. In addition, the thickness of the oxide scale in the Ti/Nb addition sample was higher than that of the BM sample.

It can be concluded that, for the BM sample, water vapour has a great influence on the mass gain and oxidation rate. A higher water vapour content gives a higher oxidation rate, resulting in a thicker oxide scale (Chen and Yeun, 2013). However, the Ti/Nb addition samples in this study had very little effect on the oxidizing atmosphere since the mass gains for 1 min and 5 min were not significantly different in spite of their oxidation rates being higher than those of the BM samples in both conditions. The addition of the Ti and Nb content alters the microstructure in microalloyed low carbon steel and can explain the reason why the Ti/Nb addition sample is less sensitive to the water vapour content than the BM sample in the oxidizing atmosphere. Our results are in the same trend as the study by Ngamkham and Chandra-ambhorn (2017), which found that the mass gain as a function of time of the Ti/Nb addition samples oxidized in pure oxygen and 17.9% water vapour with the oxygen atmosphere at 815°C for 1 min were 0.27 and 0.25 mg/cm², respectively.

Microstructure of Oxide Scale

To determine the oxide scale phase, the Ti/Nb addition samples oxidized in a humidified atmosphere and pure oxygen atmosphere at 900°C for 5 min were subjected to XRD analysis which is shown in Figure 3. For the Ti/Nb addition sample oxidized in the humidified atmosphere, the following peaks were observed: wüstite (FeO), hematite (Fe₂O₃), magnetite (Fe₃O₄), Ti-doped magnetite (Fe(Fe_{1.902}Ti_{0.098}O₄),

titanium carbide (TiC), and iron (Fe). For the sample oxidized in the pure oxygen atmosphere, the magnetite phase was predominantly observed with additional Ti-doped magnetite and titanium carbide phases. However, the peaks of the hematite were not detected possibly due to a fall off of the brittle layer during delivery. Both oxidizing atmospheres generate similar oxide phases. With a small fraction of Ti addition (0.05 wt.%), the Ti atoms, which form a reactive element, react with the oxygen and then substitute Fe in the magnetite lattice, resulting in the Ti-doped magnetite phase. The previous study by Ngamkham and Chandra-ambhorn

(2017) also found this phase in a humidified atmosphere.

Figure 4 summarizes the overall thickness of the oxide scale of the BM and Ti/Nb addition samples. Longer oxidation times establish a thicker oxide scale, as shown in Table 2. The oxide scale of the Ti/Nb addition samples forms roughly 2-3 times thicker than that of the BM samples in every condition. The water vapour does not significantly influence the thickness of the oxide scale in the Ti/Nb addition samples. The oxide scale thickness of the Ti/Nb addition samples is in range of 68-71 μm in both conditions, in contrast to the BM samples which are in the range of 20-28 μm . It could be said that the relative thickness of the Ti/Nb addition samples is significantly greater than that of the BM samples but the sensitivity of Ti/Nb addition samples is less in both conditions, as shown in Table 2.

The SEM images illustrating the grain size structure of the BM and Ti/Nb addition samples are shown in Figure 5. Both samples were oxidized in a pure oxygen atmosphere for 1 min. The average grain size of the BM and Ti/Nb addition samples are $5.86 \pm 1.57 \mu\text{m}$ and $5.05 \pm 2.23 \mu\text{m}$, respectively. It is worth noting that the oxidized atmosphere does not significantly affect the grain size. With the addition of a small concentration of the Ti and Nb contents, the Ti/Nb sample was found to have the grain size reduced by 16%, which is in agreement with a previous study by Yuan *et al.* (2015).

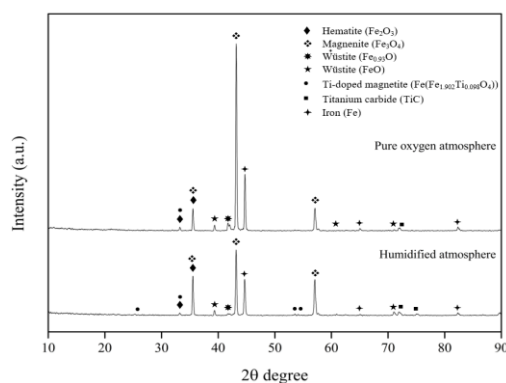


Figure 3. XRD pattern of the Ti/Nb addition sample at 900°C for 5 min in a humidified atmosphere (below) and pure oxygen atmosphere (top)

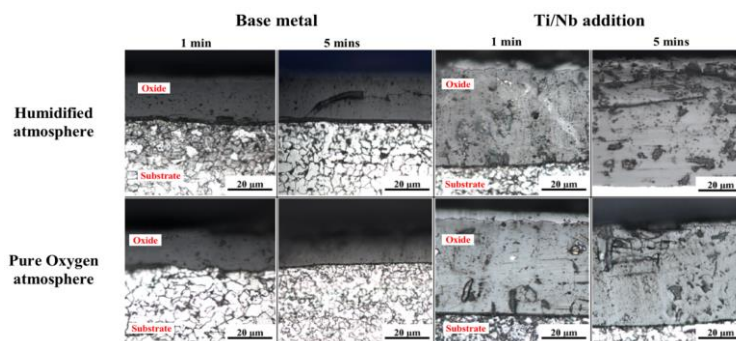


Figure 4. The oxide scale and substrate of the base metal and Ti/Nb addition samples in each condition

Mechanical Adhesion Testing

To analysis the mechanical adhesion of the thermal oxide scale on the substrate, the following 2 parameters could identify the adhesion mechanism and scale failure behavior: the percent strain of the first spallation ($\% \epsilon_{sp}$) which is the critical strain initiating spalled scale and the spallation ratio which is the area of spalled scale per total probe area. The scale adhesion on the substrate can be observed by whether the first spallation is easily detached from the substrate.

Figure 6 shows the scale failure at various strains. The strains initiating at the first spallation of the samples oxidized in the humidified atmosphere were $1.38\% \epsilon_{sp}$ for 1 min and $0.66\% \epsilon_{sp}$ for 5 min for the BM sample and for the Ti/Nb addition sample they were $0.95\% \epsilon_{sp}$ for 1 min and $1.88\% \epsilon_{sp}$ for 5 min. It could be said that the strain initiating at the first spallation in both materials was not significantly different in the humidified atmosphere. However, in the pure oxygen atmosphere, the strain initiating at the first

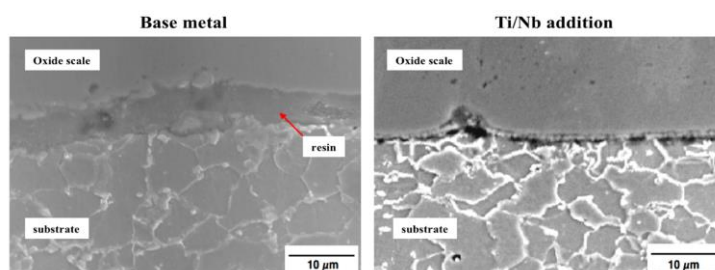


Figure 5. SEM images of the base metal (left) and Ti/Nb addition (right) samples in pure oxygen atmosphere for 1 min

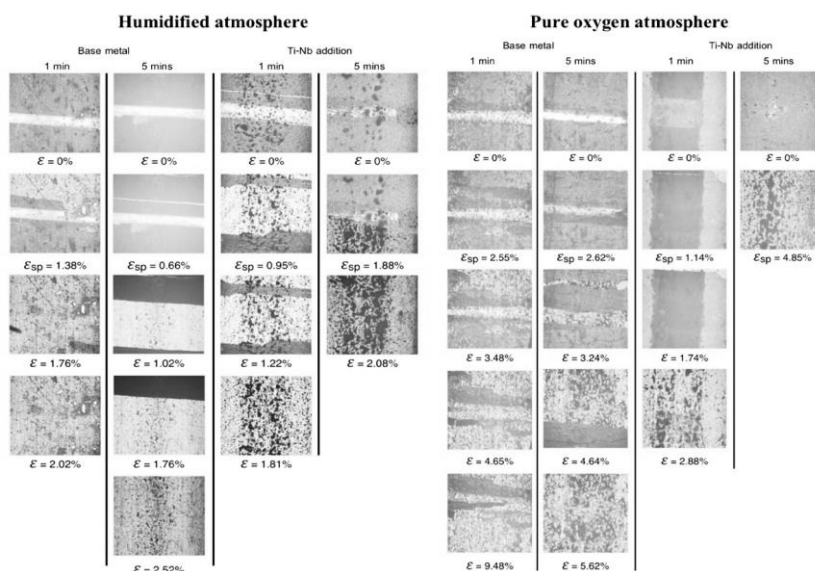


Figure 6. Evolution of scale failure with the imposed strain of the base metal and Ti/Nb addition samples in a humidified atmosphere (left) and pure oxygen atmosphere (right) for 1 and 5 min

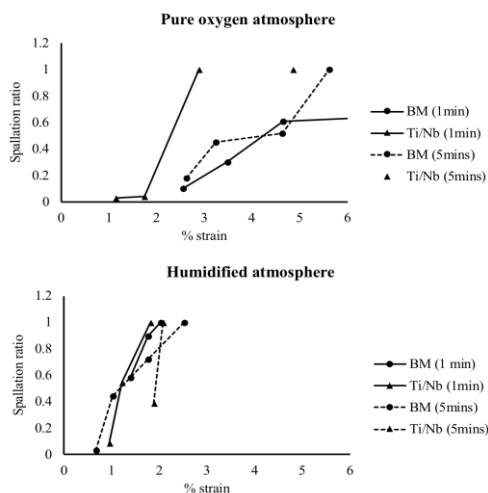


Figure 7. Spallation ratio as a function of the imposed strain in a humidified atmosphere (below) and pure oxygen atmosphere (above)

spallation is not similar in both the BM and Ti/Nb addition samples. The strains initiating at the first spallation were $2.55\% \epsilon_{sp}$ for 1 min and $2.62\% \epsilon_{sp}$ for 5 min for the BM samples and for the Ti/Nb addition samples the strain was $1.14\% \epsilon_{sp}$ for 1 min. However, the strain initiating at the first spallation for 5 min oxidizing of the Ti/Nb addition sample could not be captured, possibly due to a hanging detached scale on the surface. These results confirm that the adhesion of the oxide scale in the the BM sample was substantially affected by the humidified atmosphere. Contrastingly, the initial strain of the first spallation of the Ti/Nb addition sample was comparable in both atmospheres ($0.95\% \epsilon_{sp}$ in the humidified atmosphere and $1.14\% \epsilon_{sp}$ in pure oxygen).

There was a subsequent oxide scale failure at the imposed strain, as shown in Figure 6. It was apparent that in the humidified atmosphere the spallation of the oxide scale fell off in bigger pieces after the first spallation occurred. The spallation ratio of the oxide scale as a function of the percent strain is presented in Figure 7. The spallation ratios of the oxide scale in Figure 7 were calculated from Figure 6. The percent strains of both the

BM and Ti/Nb addition samples in the humidified atmosphere were in range of 2%, but their percent strains in the pure oxygen atmosphere were more extensive. As seen from Figures 6 and 7, the oxide scale in the Ti/Nb addition sample rapidly detached from the substrate, disregarding the oxidizing atmospheres. On the other hand, in the BM sample, the failure of the oxide scale between the 2 oxidizing atmospheres was more attached. The failure in the BM sample in the oxygen atmosphere was far more adhesive than that in the humidified atmosphere. These results indicate that the small amount of Ti/Nb addition influences the behaviour of scale adhesion. In both oxidizing atmospheres, the Ti/Nb addition showed a lower strain initiating at the first spallation than that of the BM sample, resulting in a weaker oxide scale adhesion. Our result is in good agreement with previous studies by Monteiro *et al.* (2011) and Chandra-ambhorn *et al.* (2013). They found that the adhesion of the oxide scale become more easily detached by the effect of water vapour in the oxidizing atmosphere.

Our study showed that the BM sample in the humidified atmosphere (1.38%) was more adherent than in a dry condition which is only 1.2% (Chandra-ambhorn *et al.*, 2013). However, the oxide scale of the sample oxidized in pure oxygen atmosphere shows more adhesion with the higher oxidation rate. The effect of the water vapour in the pure oxygen atmosphere is still ambiguous and needs further investigation. Even though there is limited study of Ti/Nb addition on adhesion of oxide scale, our result shows the same trend of scale adhesion behaviour as in steel.

Conclusions

In this paper, the authors have investigated the microstructure and thermal oxide scale adhesion of 0.05 wt. % Ti/Nb addition microalloyed steel and BM under a humidified atmosphere and pure oxygen atmosphere at 900°C oxidizing temperature for 1 min and 5 min. The substrate, oxide phase, and thickness of the oxide scale were investigated by OM, SEM, and XRD

analyses. The adherence of the oxide scale was explored using the tensile test. The following summaries may be drawn:

1. The oxidation rate of the Ti-Nb addition is obviously higher than that of the BM because the oxide scale of the Ti/Nb addition sample formed more thickly than that of the BM sample. For the BM sample, water vapour had a great influence on the mass gain and oxidation rate. A higher water vapour content gives a higher oxidation rate, resulting in a thicker oxide scale. However, the Ti/Nb addition sample in this study still has a minimal effect from the oxidizing atmosphere.

2. The presence of the oxide phases of the Ti/Nb addition sample shows similar phases in both 5 mins' oxidizing atmospheres. The magnetite phase was predominantly observed with additional Ti-doped magnetite and titanium carbide phases. Ti atoms react with oxygen and then substitute Fe in the magnetite lattice, resulting in a Ti-doped magnetite phase. The oxide scale thickness of the Ti/Nb addition sample formed more thickly than that of the BM in every condition. The water vapour does not significantly influence the thickness of the oxide scale in the Ti/Nb addition sample. The grain size was marginally reduced in the Ti/Nb addition sample compared with the BM sample.

3. The small amount of the Ti/Nb addition apparently influences the behaviour of scale adhesion. In the oxidizing atmosphere, the Ti/Nb addition showed a lower strain initiating at the first spallation than the BM sample, resulting in weaker oxide scale adhesion. However, the oxide scale of the sample oxidized in pure oxygen atmosphere shows more adhesion.

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