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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 550–850 °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.

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

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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 Accutum-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 °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

Table 1
Chemical compositions of the microalloyed 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.

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