OXIDATION BEHAVIOUR OF HIGH CHROME STEEL ROLLER AFTER LASER SURFACE MELTING

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Abstract. The oxidation behavior of the as-received and laser melted high chrome steels at 650 and 800 °C were studied. High chrome steel consists of tempering martensite and reticular carbides. Due to the high thermal stability and the low oxidation rate of carbides, at the beginning oxidation nucleates at the matrix-carbide interfaces and propagates in the matrix, giving rise to an uneven oxide scale. The surface of the as-received steel oxidized at 800 °C appears completely covered by the oxides, but maintains the irregular morphology. However, cracking was observed on the top layer due to growth stress and thermal stress. Laser surface melting leads to the dissolution of carbides and to the uniform distribution of carbon and alloying elements in the melted layer. The melted layer consists of fine austenite dendrites and granular $M_{23}C_6$ carbides. A homogenous oxidation occurred on the laser melted steel surface resulting in the formation of a compact and even oxide scale. The differences in the structure and the carbide volume fraction are responsible for the different oxidation mechanisms of the as-received and laser melted steels.

1. INTRODUCTION

Hot-rolling conditions have become gradually complicated and severe in many rolling plants because of the increasing amount of thin plates and high-strength steel plants [1-3]. Some of the most important segments in the operating costs of a modern hot rolling mill are related to the work rolls, since they are expensive and a large stock must be kept in hand to assure the continuous operating of the mill. Whatever the stand in the mill, the predominant wear phenomena of the work rollers remain thermal fatigue, abrasion, adhesion and oxidation [4,5].

During rolling the working conditions cause the oxidation of the roller surface which influences the performance of the rollers. Oxidation is mainly a surface-dependent degradation, and has been found significant in determining wear rate [6]. According to [7], hot rollers rolling strips to thinner gauges at higher speeds seem to benefit from the oxide formed at their surface. Continuous and even oxide scales decreases the friction coefficient between the roller and the rolled materials, prevent the heat diffusion of rollers, thus improving the surface quality of rollers and the dimensional precision of rolled materials.

Laser surface melting (LSM), as the simplest treatment method, does not involve change in the overall chemical compositions and no additional precious materials are needed. The rapid melting and solidification can lead to the formation of fine microstructures. The objective of the present work is to study the oxidation behaviors of the as-received and laser melted steels.

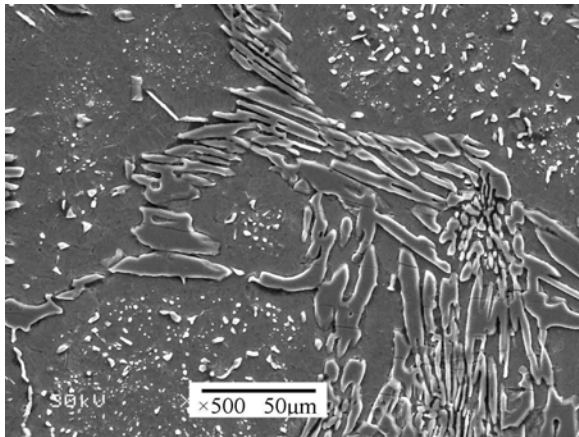Corresponding author: M.Y. Li, e-mail: lmy_102411@163.com
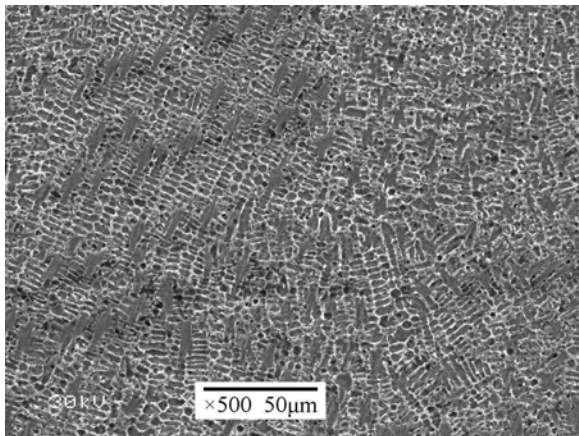
Fig. 1. Microstructure of high chrome steel.

Fig. 2. Microstructure of laser melted steel.

2. EXPERIMENTAL

High chrome steel with a chemical composition in wt.%: 1.09C, 10.48Cr, 1.24Si, 0.53Mn, 0.56Ni, 1.04Mo, 0.39V, 0.031P, 0.017S, balance Fe, was machined to the size of 20 mm×10 mm×10 mm. LSM was carried out with a power of 2.7 kW and a traverse speed of 5 mm/s. The laser beam was defocused to a spot of 3 mm in diameter. A multiple pass laser treatment, with an overlap of 1.0 mm, was made to the samples.

Surface of the specimens were polished with SiC paper up to #1200 and were ultrasonically cleaned in acetone, dried and weighed prior to oxidation. The oxidation kinetics was studied at 650 and 800 °C for 120 h. The microstructure and oxide morphologies of the as-received and laser melted steel were carried out by scanning electron microscope (SEM). The constitution of the oxidized scales were analysed by X-ray diffractometry (XRD).

3. RESULTS AND DISCUSSION

3.1. Microstructural analysis

High chrome steel consists of tempering martensite and a noticeable volume fraction of M_7C_3 carbides (Fig. 1). The continuous carbide network is located in the grain boundary, which reduce the ductility [8]. LSM leads to the complete dissolution of reticular carbides and the laser melted layer consists of ultrafine dendrites of austenite and interdendritic $M_{23}C_6$ carbides [9], as shown in Fig. 2.

3.2. Characterization of the oxidized specimens

The phase constituents of the specimens oxided at 650 and 800 °C for 120 h are shown in Fig. 3, which are representative of the constitutions present at or closing to the top surface. At 650 °C Fe_2O_3 and Fe are revealed on both surfaces of the as-received and laser melted steel, whilst for the as-received specimens, the XRD pattern exhibits relative high Fe peaks intensities. Moreover, the phases present on the oxide scales of laser melted steel at 650 °C
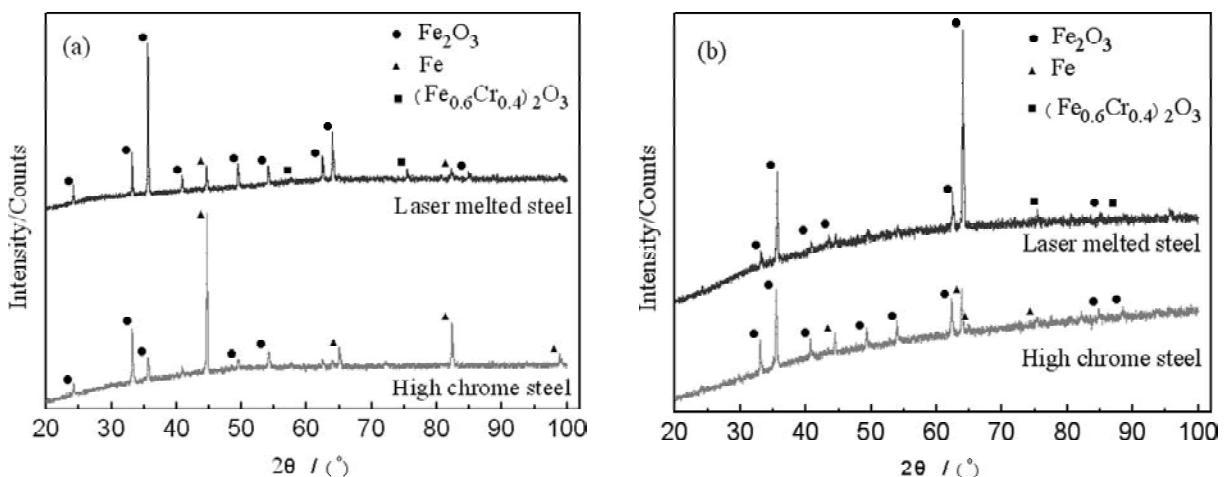

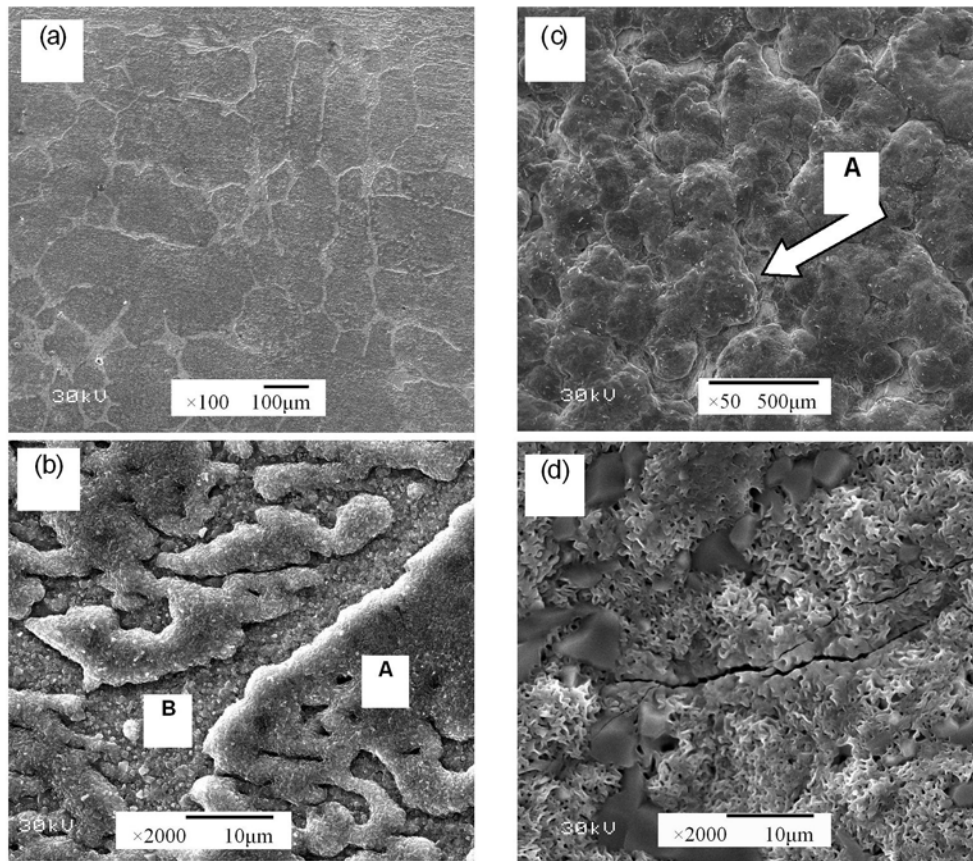**Fig. 3.** XRD spectrums of the sample oxidized of (a) at 650 °C; (b) at 800 °C.

Fig. 4. Oxide morphology of the as-received high chrome steel oxided for 120h. (a) at 650 °C at low magnification; (b) at high magnification; (c) at 800 °C; (d) cracking of the oxide scale.
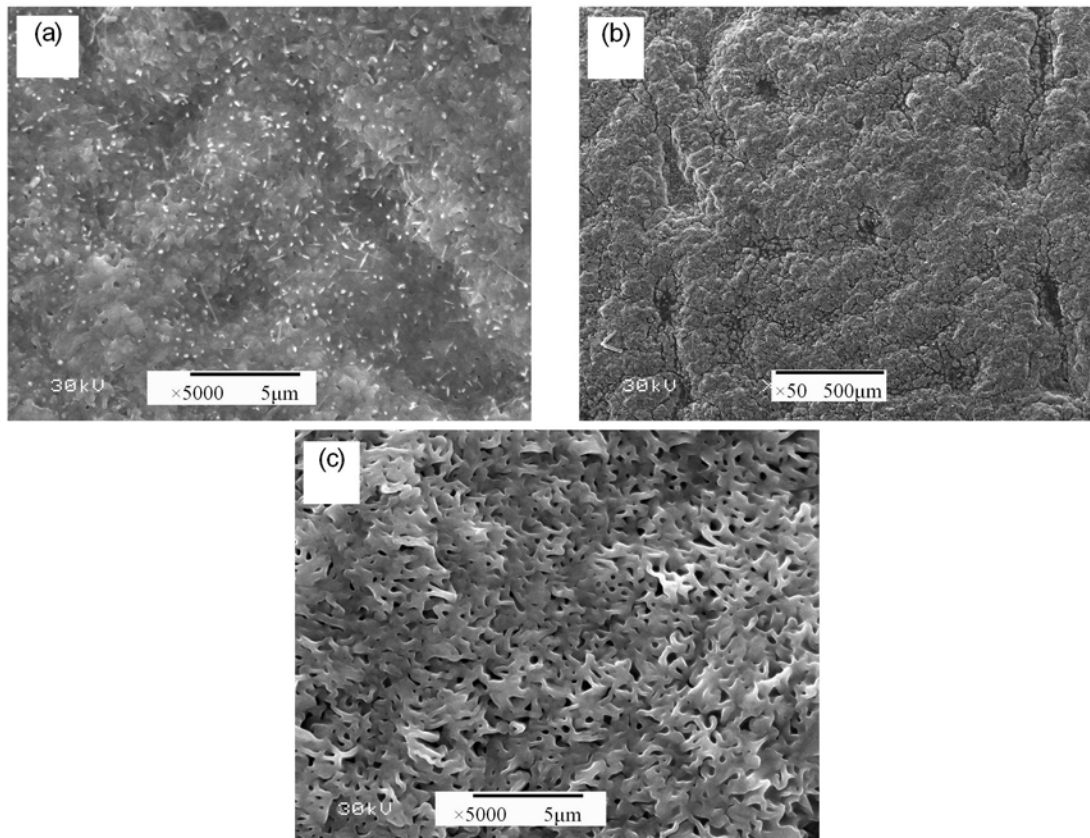

Fig. 5. Oxide morphology of the laser melted steel oxided for 120h. (a) at 650 °C; (b) at 800 °C at the low magnification; (c) at the high magnification.
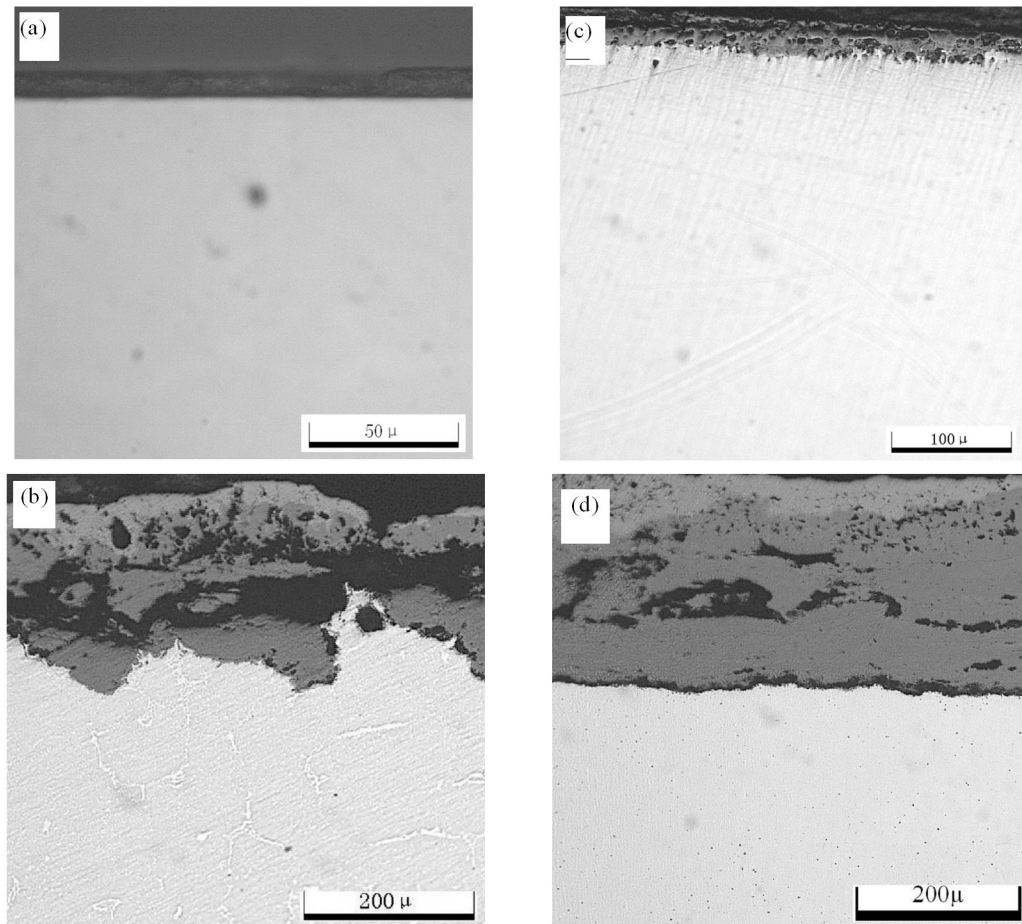
Fig. 6. Cross-sectional micrographs of oxide scales. (a) high chrome steel at 650 °C; (b) at 800 °C; (c) laser melted steel at 650 °C; (d) at 800 °C.

are identified to be Fe_2O_3, $(Fe_{0.6}Cr_{0.4})_2O_3$ and Fe while Fe peaks disappear at 800 °C.

Fig. 4 shows the morphology of the oxidized surfaces of the as-received steel at the two temperatures. As it can be seen, because of the high oxidation resistance of carbides, a selective oxidation of the matrix occurs (Fig. 4a and A zone), which forms an irregular scale. In fact it is lower at B zone in correspondence to the large carbides, thus negatively influencing the compactness and homogeneity of the oxide scale on the surface. The surface oxidized at 800 °C appears completely covered by the oxide scales, but still maintains the irregular morphology (Fig. 4c).

The oxide morphologies of the laser melted steel after oxidizing at 650 °C and 800 °C were revealed in Fig. 5. As it is can be seen, the oxide scales produced on the surface of the laser melted steel are very uniform and smooth. At high magnification it can be seen that the oxidation products are finer than those produced on the surface of the as-received steel shown in Fig. 5c.

The thickness increases with the oxidation temperature, as shown in Fig. 6 relevant to the as-re-

ceived and laser melted steels at 650 and 800 °C. In particular the thickness at 650 °C is less than 5 μm, thus allowing the substrate XRD peaks to be detected. The thickness of the oxide scale is not even on the whole surface of high chrome steel, in particular at 800 °C. In fact it is thin in correspondence to the carbides. Besides, the interface between the oxide scale and the matrix is irregular (Fig. 6b) but is very even in case of the laser melted steel shown in Fig. 6d.

3.3. Oxidation kinetics

Fig. 7 shows the mass gain curves of the oxidation for 120 h at different temperatures. It is well evident that the oxidation increases with temperature as expected. However, the laser melted steel has a slight higher oxidation rate than the as-received steel. At 650 °C the two steels follow an oxidation kinetic with a logarithmic trend (Fig. 7a), and with a parabolic function at 800 °C (Fig. 7b). At the two temperatures the as-received steel has a slightly lower oxidation rate than the laser melted steel. That does not mean that the oxidation resistance of the as-
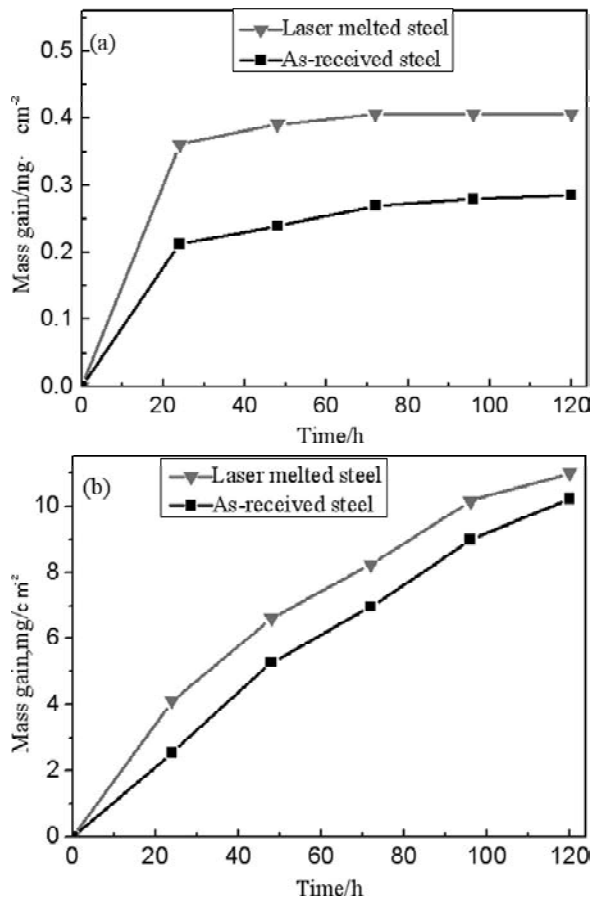
Fig. 7. Oxidation kinetics curves (a) at 650 °C; (b) at 800 °C.

Fig. 8. Schematic illustration of oxidation mechanism (a)-(d) high chrome steel; (e)-(f) laser melted steel.

receives steel is higher, but may be connected with the uneven oxidation on the surface of high chrome steel (Fig. 4).

3.4. Oxidation mechanism

At high temperature oxidation can occur by direct reaction with the air. This is a type of corrosion, referred to as high temperature oxidation. In the case of high chrome steel, at the initial stage both oxygen and metal ion concentration are sufficient and thereby interface reaction is the controlling step for oxidation. Oxidation nucleates at the carbide-matrix interface due to the high free energy content by surface reaction (Figs. 8a and 8b). Because of the high thermal stability and the low oxidation rate of M_7C_3 carbides, oxide grows mainly on the metal matrix, giving rise to an uneven oxide scale. After an oxide film has formed on the surface, growth is limited by the diffusion of ions through the oxide layer, tending to cover the whole surface, but it maintains the irregular morphology even (Figs. 8c and 8d). In addition, cracking was observed on the top layer in Fig. 4d due to growth stress, thermal
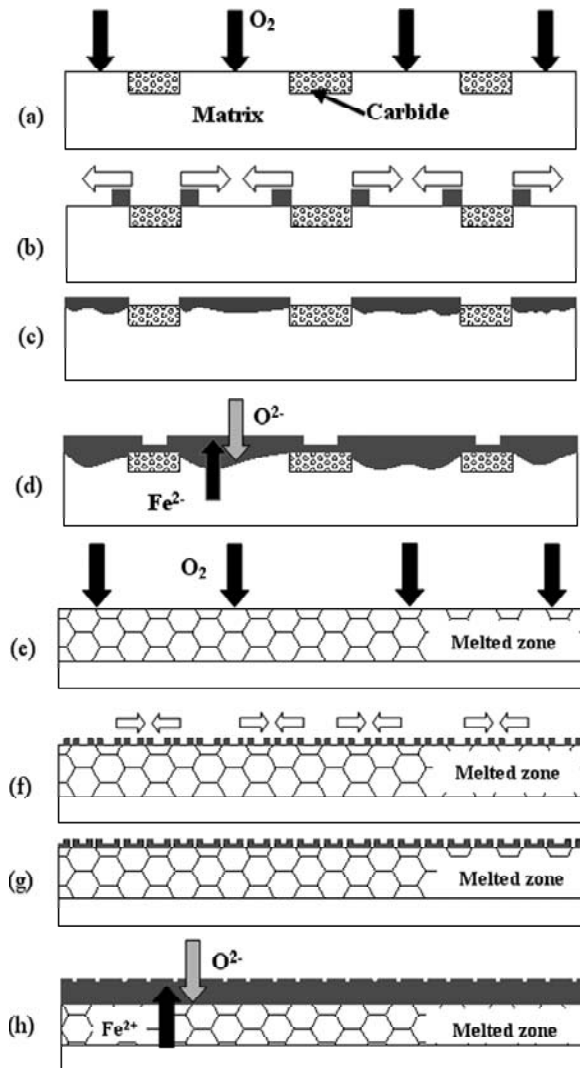
stress, *etc.* As it is known, the growth stress is mainly resulted from the volume changes of the matrix and carbides, since the density of the oxide scale is seldom the same as that of the metal. Besides, there exists great difference in expansion coefficients between the matrix and oxide scale. The stress relaxation of the oxide scale can not be completed by plastic deformation but cracking or spalling [10,11]. In this way, they create some diffusion paths and facilitate internal oxidation of the roller matrix, negatively affecting the roller profile.

The fine and homogeneous microstructure was formed in the laser melted layer. At the initial stage, interface reaction dominates and preferential oxidation occurs at the grain boundary. When the scale reaches a given thickness with increasing exposure time, the process of oxidation in the laser melted

steels is restrained and precludes internal oxidation, thus metal ion transport becomes the control step. The Fe^{2+} in the laser melted samples tends to diffuse outward from the substrate to the external oxide-air interface and form the oxides (Fig. 8e). The outward diffusion of cations is complemented by solid-state dissolution and diffusion of oxygen from air into the alloyed zone through the oxide scale. Higher temperature (800 °C) accelerates the diffusion and leads to the thicker oxide scale (Fig. 8f). The parabolic trend of the oxidation curve corresponds to the restraint of the ionic diffusion.

Due to the solid solution strengthening of carbon and alloying elements, austenite in the laser layer has a high thermal stability. Once formed, the oxide scale is well supported by the laser melted layer with high thermal stability and strength as well as toughness, precluding the propagation of cracks and spalling. The compacted and even oxide scale present at high temperature play a role of solid lubricant by forming glazed surfaces and reduce sticking [12]. Furthermore, they contribute to the enlargement of the wear track that increases the contact surface and therefore decreases the strain and the friction coefficient [13].

4. CONCLUSIONS

Laser surface melting leads to significant microstructural refinement of high chrome steel, removing the interconnected eutectic carbide and reducing the grain size. The laser melted layer was composed of fine austenite dendrites and granular $M_{23}C_6$ carbides. As the temperature increases, the corrosion rate increases significantly. In the case of high chrome steel, at the beginning oxidation nucleates at the matrix-carbide interfaces and propagates in the metal matrix, giving rise to an uneven oxide scale. The surface of the as-received steel oxidized at 800 °C appears completely covered by the oxides, but maintains the irregular morphology. However, cracking was observed on the top layer due to growth stress and thermal stress. LSM leads to the dissolution of large primary carbides and to the uniform distribution of carbon and alloying elements in the melted layer. A homogenous oxidation occurred on the laser melted steel resulting in the formation of a compact and even oxide scale.

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