Oxidation Kinetics Researches under the Condition of Compressive Loading

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Abstract. High temperature oxidation behavior of alloys is mostly affected by an external loading. The growth of oxide scale, oxide products, interfacial reactions and other characteristics have been affirmed to be affected by the external loading. Here, it provided the oxidation kinetics of several metals under the compressive loading. And the growth of oxide scale was distinguished in the form of thin oxide layer and thick oxide layer. Different compressive effect on the growth of oxide scale was summarized. At the initial oxidation stage, the applied compressive stress induced more defects on the surface of alloy, supplying more oxide nuclei, thereby increased the growth of the thin oxide layer. In the case of the growth of the thick oxide layer, it was attributed to the short circuit paths of the oxide grain boundary inherited from the initial oxidation stage and the cracks or other defects deduced by the applied compressive stress. Thus the oxide kinetics of alloys was promoted. However, considering the interfacial reaction at scale/metal, the coarsens of vacancies would occur after a long time of oxidation, decreasing the growth of oxide scale.

1. Introduction

The oxidation resistance of alloys is reflected by oxidation kinetics, and oxidation rate constant is close related to the application lifetime of alloys. Commonly, the growth of Cr, Al, Si-formed integrity oxide scale is slow, which can play a role of protection to alloys [1]. However, the alloys are always used in various serious environment in the practice application. Thus the oxide scale on the alloys will be destroyed, and cracking and even spallation are occurred. Once the further healing oxidation cannot supply the protective oxide scale, the alloys will be oxidized in a fast rate. Especially, the oxide scale is prone to spall under the external loading conditions, which brings a negative effect on the oxidation kinetics [2]. More and more investigations have been carried out to explore the effect mechanism of external loading on the growth of oxide scale. Nowadays, there are still controversy about the effect mechanism. Most studies suggested that the growth of oxide scale was increased by the external loading [3-5]. Several investigations reported that the oxidation rate was decreased by the loading [6,7]. And a few experiments affirmed that no effect of loading on the growth of oxide scale [8]. Undeniably, the external loading has a fatal effect on the brittle oxide scale. Once the oxide scale is broken, the slowly growth of integrity oxide scale is interrupted. Therefore, the explore on the oxidation kinetics of alloys under the external loading is very important. The authors reviewed the
studies of oxidation kinetics of several metals under the compressive loading, and the effect mechanism was summarized.

2. Oxide-scale growth characteristics under compressive loading

Oxidation of a metal/alloy occurs owning to the reaction with an oxidizing atmosphere under the driving force of the free energy of the oxide formation. A continuous oxide scale as a barrier to decrease the fast depletion of metal can form on the surface of the metal. However, the growth of oxide scale will be affected when subjected to an external loading condition. The growth rate of oxide scale is depended on the oxidizing time, the integrity of oxide scale, and other factors. In order to clarify the effect of external loading on the growth of oxide scale, a schematic of oxide-scale evolution under the external loading is shown in Figure 1. In the short-stage oxidation, a thin film will form on the surface of the metal shown in Figure 1(a), and the growth of the thin film would be affected by the loading. In fact, it is indeed affected according to the previous studies [2]. With the time increasing, the oxide scale is gradually thickened, as indicated in Figure 1(b). As the PBR and the mechanical nature of oxide scale, the oxide scale would be bulking, cracking and spalling. The continuous growth of oxide scale is then damaged, as shown in Figure 1(c) and Figure 1(d). As for the destroyed oxide scale, its growth is depended on the healing behavior of further oxidation at the naked metal surface. It is concluded that the growth of a metal/alloy under the loading condition is consisted of two stages, i.e., the growth stage of thin oxide scale and the growth stage of thick oxide scale. And the growth behavior of thick oxide scale is depended on the mechanical nature of oxide scale, which can be comprised of two forms of buckling and spalling oxide scale. Therefore, the following summary of the effect of compressive stress on the growth of oxide scale of metal/alloy is based on this distinctive.

Figure 1. Oxide-scale growth characteristics under compressive loading: (a) thin oxide-scale formation; (b-d) thick oxide-scale continuous formation; (b) protective oxide-scale growth; (c) oxide-scale failure model I: decohesion and buckling precede through-scale cracking; (d) oxide-scale failure model II: through-scale shear cracking precedes interfacial decohesion [9]

3. Oxidation kinetics under compressive loading

3.1 Thin oxide-scale growth stage

Early stages of oxidation of a metal/alloy typical are consisted of nucleation and growth of nuclei and then a continuous thin layer of oxide. During this stage, the involved oxidation kinetics is close related to the surface condition of metals. Selective oxidation and short-circuit diffusion would occur at the local surface of metals where high subsurface dislocation density and lots of defects are existed [2]. And subsequently fined oxide particles would form, which enhances the effective diffusion according to the equation 1.

\[ D_{\text{eff}} = (1 - f) D_b + f D_{gb} \]  

(1)

Where \( D_{\text{eff}} \) is effective diffusion coefficient, \( D_b \) is diffusion in the bulk, \( D_{gb} \) is diffusion along grain boundaries, \( D_{gb} \gg D_b \) [10]. Thus, the induced dislocations and defects by some methods will supply more nuclei and increase the diffusion, and therefore increase the oxidation rate of a metal/alloy.
According to previous investigations, external loading, such as grinding, sandblasting and even directing loading, can introduce dislocations and defects [2]. Especially, the growth behavior of oxide scale is dependent on the mechanical loading.

Figure 2 shows the evolution of instantaneous oxidation rate constant with increasing time of pure Ni and Fe-20Cr when subjected to compressive loading. It can be seen that compressive loading increase the initial oxidation rate for pure Ni oxidized at 800 °C and Fe-20Cr alloy oxidized at 900 °C respectively, as shown in Figure 2(a) and Figure 2(b). That is related to the short-circuit diffusion of grain boundaries, which can be supported by the evolution of oxide particles during such process.

**Figure 2.** Instantaneous oxidation rate constant with increasing time of (a) pure Ni oxidized at 800 °C and (b) Fe-20Cr alloy oxidized at 900 °C

Figure 3 displays the surface morphologies of pure Ni oxidized at 800 °C and Fe-20Cr oxidized at 900 °C. As can be seen, compressive loading induced the change of surface morphology of pure Ni from classical ridge-like under unstressed condition displayed in Figure 3(a) to particle-like in the case of 20 MPa shown in Figure 3(b). As for Fe-20Cr alloy, the compressive loading made the oxide size more smaller (by comparing the oxide particles under 0 MPa stress in Figure 3(c) and 5 MPa stress in Figure 3(d)). Above evolution of surface morphologies of both metals implies that the instantaneous oxidation rate constants are related to the grain size of oxide. And the smaller grain size of oxide induced by the compressive loading can be as an ex situ evidence on the increasing nuclei at the introduced dislocations and defects. This phenomenon is also reflected in pure Ni oxidized at 700 °C and Fe-16Cr alloy oxidized at 900 °C under the condition of compressive loading [10-13].
3.2 Thick oxide-scale continuous growth stage

After the formation of a thin layer of oxide, the continuous growth of oxide scale to form a thick layer is commonly controlled by the diffusion of cationic or anionic species through the oxide scale. The diffusion behavior through the oxide scale is strongly affected by the nature of oxide scale. The mechanical properties, microstructures, pores and defects of oxide scale is directly affect such diffusion process [1], which increased the difficulty for analysing the compressive loading on the growth of oxide scale. In order to simplify and scientize, the growth behavior of a metal/alloy under compressive loading is distinct according to Figure 1.

3.2.1 growth of integrity oxide scale. For the growth of an integrity oxide scale, it is mainly closed to the diffusion of cationic or anionic species through the oxide scale and the interface reaction at the oxide/metal interface. In particular, the change of oxide products will occur owing to the external loading. That affects the diffusion behavior in the oxide scale. Though some different mechanisms has been proposed, it did not reach a consensus on the effect of external loading on the change of oxide products [14,15]. In the present work, pure Nickel, which have no change of oxide product during the oxidation and is widely used to investigate the oxidation mechanism under various conditions owing to classical and simply oxide product, were chosen to study the growth behavior under the compressive loading.

Figure 4 shows the parabolic oxidation curves of pure Ni oxidized at 700 °C under different compressive conditions. As can be seen, the applied compressive loading increase the growth of pure Ni. Besides, different laws was observed. It completely followed a parabolic law for conventional oxidation. However, it followed a two-stage parabolic law in the case of 10 MPa compressive loading. Interestingly, it did not follow parabolic law subjected to 20 MPa compressive loading. In order to clarify that, the cross-sectional morphologies were examined.
Figure 4. Weight gain as a function of the square root of time for Ni oxidized at 700 °C subjected to compressive loading [12].

Figure 5 shows the cross-sectional morphologies of pure Ni oxidized under different conditions. It can be seen, by comparing the cross-sectional morphologies of pure Ni oxidized at 700 °C and 10 MPa and 20 MPa for 20 h as shown in Figure 5(a) and Figure 5(b), that obvious coarsens of pores at the oxide/metal interface were generated. According to the relations between the growth of oxide scale and vacancy concentration proposed by Gibbs [16], which was proved by Stroosnijder [17],

\[
dx / dt = B \Omega p_{o_j}^{-1/2} [(V_L)_e / (V_L)^{2/n}] (D_L / x)\]  \( (2) \)

Where \( \Omega \) is volume of oxide per metal ion, \( (V_L)_e \) is thermodynamic equilibrium concentration of lattice vacancies in a metal; \( V_L \) is concentration of lattice vacancies close to the scale/metal; \( D_L \) is cation diffusion coefficient in oxide; \( x \) is thickness of oxide scale; \( n \) and \( B \) are constants. It can be gained that coarsens of pores substantially increase the vacancy concentration at the oxide/metal interface, which decrease the oxidation rate. It can be explained that the parabolic oxidation rate at second stage is smaller than that at the initial one in the case of 10 MPa compressive loading. It is because that the growth of pores continuously decrease the oxidation rate. It displays more obvious in the case of 20 MPa, even no parabolic law was followed, and the oxidation rate gradually decrease with the time. So, it can be detected that the oxidation rate in the case of compressive loading will lower than that of the conventional test in the following oxidation time. Figure 6 shows the growth of oxide scale for pure Ni up to 140 h. It can be seen that the weight gain for the conventional test was higher than that under 10 MPa compressive loading after about 60 h. As for the increasing oxidation rate before 60 h, it was related to the nucleation, growth of nuclei and thin layer. The change of surface morphologies were approved that in the previous work [11-13]. Besides, the growth of integrity oxide scale on Fe-20Cr alloy was increased by compressive loading based on the short-circuit diffusion along oxide grain boundary [10].

Figure 5. Cross-sectional morphologies of pure Ni oxidized at 700 °C under (a) 10 MPa and (b) 20 MPa for 20 h [11]
3.2.2 growth of cracking oxide scale. The growth of cracking oxide scale under the compressive loading is dominated by short-circuit diffusion, such as grain boundary, cracks, pores and other defects. Such process shows that the growth of oxide scale was increased by compressive loading. As seen in Figure 7, the growth of oxide scale on pure iron was increased by compressive loading. Because the oxide products of pure iron at above 570 °C are consisted of haematite, magnetite and more amount of wustite phases, the oxide scale is prone to crack under the loading owing to the poor mechanical properties of wustite layer [1]. The short-circuit diffusion along the cracks and other defects becomes the main mechanism of oxidation of pure iron under the compressive loading. Figure 8 shows the surface morphologies of pure iron after 20 of oxidation under loading. And the surface morphology of pure iron oxidized at 650 °C for 20 h under 6MPa compressive stress is shown in Figure 8 (a). It can be seen that buckling, cracks and local spallation were displayed, which become the short-circuit diffusion paths. And high magnification surface morphologies show that a lot of pores in the oxide scale were generated in comparison with unstressed condition and 6 MPa compressive stress, as displayed in Figure 8(b) and Figure 8(c). Oxygen then can directly reach the reaction interface, rather than through the diffusion process. Those can greatly increase the growth of oxide scale, as shown in Figure 7, the weight gain substantially increases after 10 h of oxidation under 6 MPa loading.

Figure 6. weight gain as a function of time for pure Ni oxidized at 700 °C

Figure 7. weight gain as a function of time for pure iron oxidized at 650 °C [18]
A Fe-16Cr alloy, which formed multi-layer oxide, was chosen to explain the effect of compressive loading on the growth of oxide scale. As can be seen, the growth of oxide scale on the Fe-16Cr alloy followed a parabolic law in the presence of compressive loading. And the compressive effect on the oxide scale induced its growth, as shown in Figure 9. According to the growth mechanism of Fe-Cr alloys with about 15% Cr content, commonly an outer Fe-oxide layer, a media FeCr₂O₄ layer and inner Fe(Fe,Cr)₂O₄ layer will form [1]. And the diffusion of cations or anions across the oxide scale is blocked by FeCr₂O₄ layer and inner Fe(Fe,Cr)₂O₄ layer. If the Fe-oxide layer is prone to crack, then more short-circuit diffusion paths will generate to increase the growth of oxide scale. Seen form Figure10, it can be gained that Fe-oxide multilayer and Cr-rich oxide layer was the critical characteristic of Fe-16Cr alloy. The previous investigation showed that the increased Fe-oxide layer by the loading was the important factor on the compressive effect on the whole growth of oxide scale [19]. Then, it comes a conclusion that the poor mechanical property of oxide scale is easily to induce the short-circuit diffusion paths by the compressive loading, which is one important mechanism for the growth of oxide scale.

Figure 8. surface morphologies of pure iron oxidized at 650 °C for 20 h under compressive loading of (a) 6 MPa; (b) 0 MPa; (c) 6 MPa [18]

Figure 9. square of thickness of oxide scale as a function of time for Fe-16Cr alloy oxidized at 900 °C under compressive loading [19]
Figure 10. Elemental mapping of Fe-16Cr alloy oxidized at 900 °C under 5 MPa loading for 10 h [19]

Besides, the short-circuit diffusion paths in outer Fe-oxide layer can affect the growth of internal oxidation in a Fe-20Ni alloy. Figure 11 shows the growths of intragranular (as shown in Figure 11(a)) and intergranular (as displayed in Figure 11(b)) scale for the Fe-20Ni alloy oxidized at 800 °C and 900 °C for 20 h. As can be seen, the growths of intragranular and intergranular scale are both increased by the compressive loading for the Fe-20Ni alloy oxidized at 900 °C. At 800 °C, the compressive effect on the growths of both scales is not obvious. It is implied that the effect on the growths of intragranular and intergranular scale are dependent on the applied loading and temperature.

4. Summary

The growth of oxide scale of alloys under external loading is indeed affected, although different mechanism and effect are suggested. The present review only show the compressive loading on the growth of oxide scale on several metals. Both stages of growths of oxide scale by the effect of compressive loading are displayed. At the stage of growth of thin oxide layer, the loading introduces more defects on the subsurface of metals, which increases the oxide nucleation and thereby fined oxide grains form. Short-circuit diffusion along the oxide grain boundary is modified, and the growth of thin oxide layer is increased by the compressive loading. At the stage of growth of thick oxide layer, the mechanical properties of oxide scale become the critical factor on the compressive effect on the growth of oxide scale. For the oxide scale with good ductility, such pure Nickel, the compressive loading induces the pores generation at the oxide/metal interface, and finally decreases the growth of oxide scale of pure Nickel, although the growth of oxide scale is increased by compressive loading for a 20-hour oxidation. For the oxide scale with poor mechanical property, the oxide scale is prone to cracking, buckling and spallation by the compressive loading, short-circuit diffusion paths are more increased. And the growth of oxide scale is increased, even the internal oxidation is also increased.

Acknowledgments

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