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Chemo-mechanical coupling effect in the high-temperature oxidation of metal materials: A review

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The metal materials are susceptible to be oxidized when they are exposed to the complex and harsh environments, especially at the elevated temperature. The development of corresponding chemo-mechanical coupling theory is indispensable in theoretically and numerically predicting the material properties reduction and failures due to the oxidation. In this paper, we review the historical sketch of the coupling theory of chemical reactions and mechanics in the high-temperature oxidation of metal materials. The oxidation results in the stress generation while the generated stress in turn affects the chemical reaction rate and the diffusion process of the reactants. It is therefore a complex chemo-mechanical coupling problem. This review begins with the discussion of the diffusion-controlled oxidation, and then discusses the stress-dependent diffusion during the oxidation and the oxide growth induced stress, and ends with the discussion of interaction between chemical reactions and stress. This review of chemo-mechanical coupling literature is not exhaustive; we review much of the fundamental literature and draw comparisons of coupling theory development in the filed of metal oxidation.

oxidation, diffusion, growth stress, chemo-mechanical coupling, metal

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1 Introduction

Metals are widely used as structural materials in modern industry due to their unique physical and mechanical properties. However, being reactive in nature, metals are usually susceptible to be oxidized in ambient oxygen or water, even at room temperature. Due to the huge growth stress developed in the oxide film during the oxidation, not only is the strength of material greatly reduced but also the bulking, cracking and even spalling of the oxide film occurs. This further leads to acute alteration in the chemical and mechanical properties and decreases in functionalities of host metal materials. For this reason, such phenomena attract much attention in the past decades. The theory regarding the origin of growth stress was firstly proposed by Bedworth and Pilling [1]. Then, more and more new theories were proposed. Nevertheless, these theories can be roughly categorized into two types, i.e., one-way coupling effect and fully coupling effect. For the former, only is the effect of the chemical reaction on the stress considered. For the latter, the interaction of stress, diffusion and chemical reaction is taken into account. In this paper, we review the research progress of the chemo-mechanical coupling effect in high-temperature oxidation of metal materials.

The remaining manuscript is organized into the following major topics. Sect. 2 discusses the diffusion-controlled oxidation. Sect. 3 introduces the stress-dependent diffusion during the oxidation. Sect. 4 analyzes the stress induced by

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oxide growth. Finally, the interaction between the stress and chemical reactions is discussed in Sect. 5.

2 Diffusion-controlled oxidation

The formation of oxide film on the metal surface can separate the oxygen and metal. Therefore, whether the oxide layer continuously grows or not is usually believed to be dependent on the diffusion of ions in the oxide layer such as metal and oxygen ions. For example, Young et al. [2] studied the formation of Cr_2O_3 under different oxygen partial pressures. Under low oxygen partial pressure, it was found that the oxide layer exhibits n-type semiconductor behavior while it exhibits p-type semiconductor behavior under high oxygen partial pressure. The service environment of metal materials is usually high oxygen partial pressure, thus the oxide layer exhibits p-type semiconductor behavior. As a result, it is reasonable to believe that the oxidation rate is controlled by the diffusion of ions.

Figure 1 [3] schematically shows the ion diffusion mechanism in the oxide layer proposed by Atkinson and Taylor [4]. They quantitatively confirmed that the oxidation rate of nickel at 500°C–800°C is controlled by the diffusion of nickel along the grain boundary in the oxide film. Moreover, Tsai et al. [5] established a chromia film growth model based on the oxygen-chromium counter diffusion. Rhines and Wolf [6] also proposed that the metal-oxygen counter diffusion causes the growth of the oxide layer. Kirkendall effect [7] shows that the diffusivities of the two species in binary solid solutions are different. This indicates that diffusion occurs by the vacancy mechanism. In the oxidation processes, the ions diffuse through the oxide scale by vacancy mechanism, so the diffusivities of the oxygen ions and the metal ions are not equal. Thus the location of the newly formed oxide provides further evidence for the diffusion-controlled oxidation process. When the diffusion rate of metal ions is faster, the formed oxide is mainly located near the oxygen-oxide interface in the oxide layer. On the contrary, when the diffusion rate of oxygen ions is faster, the formed oxide is mainly located near the oxide-substrate interface in the oxide layer. For example, the diffusion rate of oxygen is about three orders of magnitude smaller than that of chromium [8]. As a result, the formed chromia is mainly located near the oxygen-oxide interface in the oxide layer. Such was further confirmed by O'Keeffe and Moore [9]. They found that the diffusion rate of oxygen is several orders of magnitude smaller than that of nickel in nickel oxide, and the newly formed nickel oxide is also mainly located near the oxygen-oxide interface in the oxide layer. For the case in which the metal ions diffuse faster, a large number of vacancies form in the metal near the oxide-substrate interface. The vacancies then agglomerate to form voids, which reduces the bonding strength of the interface.

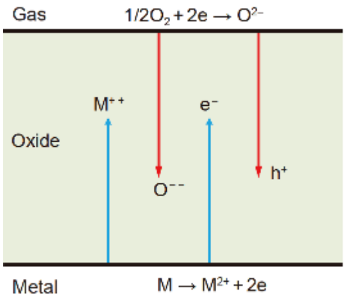

Figure 1 (Color online) Schematic diagram of diffusion mechanism, reproduced from ref. [3].

Based on the diffusion-controlled oxidation mechanism, Wagner [10] firstly established the growth theory of thick oxide film. With this theory, the oxide film growth rate can be correlated with other measurable transport properties of the oxide film, such as the diffusion coefficient. Prior to this theory, it has been observed that the growth of oxide films obeys parabolic kinetics [11]

$$h_{\mathrm{ox}}^2 = k_{\mathrm{p}} t, \tag{1}$$

where h_{ox} and k_{p} are the oxide film thickness and the parabolic rate constant, respectively; t is the oxidation time. The parabolic kinetics is consistent with diffusion-controlled oxidation with the ions concentration gradient as the driving force. As the oxide film thickens during the oxidation process, the growth rate decreases by following:

$$\frac{\mathrm{d}h_{\mathrm{ox}}}{\mathrm{d}t} = \frac{k_{\mathrm{p}}}{2h_{\mathrm{ox}}}. \tag{2}$$

3 Stress-dependent diffusion

The oxidation process of the metal material is controlled by the ion diffusion process in the oxide layer. Although diffusion is thought to be unaffected by stress in some studies, the importance of stress-diffusion interactions has attracted more and more attention in simulating the oxidation processes. Based on the thermodynamics, Li et al. [12] established the chemical potential of the mobile and immobile components in solids subjected to a non-uniform stress field. Subsequently, Koehler [13] studied the influence of lattice strain, caused by defects such as precipitation and dislocation, on the saddle-point configuration during the diffusion process. Their calculations showed that the migration energy of vacancies can be changed by 10% due to the influence of stress. Therefore, the stress affects the defect migration in at least two fundamental aspects [13–15]. One is the thermodynamics effect, which can be attributed to the dependence of the chemical potential on the stress. The other is the kinetic effect, which results from the effect of the stress on the diffusion migration barrier. Since the volumetric strain is generated by the formation volume and migration volume of the defect, the local elastic energy directly affects the diffusion. Therefore, both the stress-dependent chemical potential and the kinetic parameters controlling diffusion should take into account the effect of stress on the volume changes. For simplicity, the stress slightly affects the kinetic parameters of diffusion so that its effect can be neglected, and the formation volume of defect is greater than the volume change associated with migration such that the latter can be also neglected [16]. Some studies were also carried out to reveal the effects of stress on the formation and migration energies of defects, for example, Olmsted et al.'s [17] molecular dynamics simulation work.

Li et al. [18] were the first one who used the chemical potential gradient of point defects as the driving force for the diffusion of defects in solids with non-uniform stress field. For the point defect diffusion problem, the diffusion potential gradient should be used as its driving force. However, for dilute defect concentrations, the diffusion potential and the chemical potential are equal and indistinguishable [19]. Li et al. [12] developed Maxwell's type expressions of chemical potential, stress, strain and concentration. Later, Larché and Cahn [20] developed a diffusion potential as a function of local stress states based on the integral of Maxwell's type expressions [21].

For oxides in the form of MO, the stress-dependent diffusion potential of the ions in the lattice is generally expressed as [20]

$$\mu_s(\rho_s,\sigma)=\mu_s(\rho_s,0)-V_m\eta_{ij}^{s}\sigma_{ij}-\frac{V_m}{2}s_{ijkl}^{s}\sigma_{kl}\sigma_{ij}, \tag{3}$$

where $\mu_s(\rho_s,0)$, V_m and σ_{ij} are the stress-free diffusion potential, the molar volume of the solid and the Cauchy stress, respectively. $\eta_{ij}^{s}=\dfrac{\partial\varepsilon_{ij}^{s}}{\partial\rho_s}$, $s_{ijkl}^{s}=\dfrac{\partial S_{ijkl}}{\partial\rho_s}$ and ρ_s are the chemical expansion coefficient, the change of compliance caused by the concentration change of defect species s and the molar fraction of defect species s, respectively. ε_{ij}^{s} and S_{ijkl} are the strain produced by the concentration change of the defect species s and the compliance of the material, respectively.

It can be seen from eq. (3) that two material parameters η_{ij}^{s} and s_{ijkl}^{s} are introduced in the stress-dependent diffusion potential. η_{ij}^{s} represents the eigenstrain (i.e., stress-free strain) due to the local composition change, and is also known as the chemical expansion coefficient. The chemical expansion coefficient is similar to the thermal expansion coefficient and represents the strain caused by the change per unit concentration. s_{ijkl}^{s} represents the change of the compliance matrix caused by the change in composition. It should be noted that the compositional strain generally needs to follow Vegard's law, which states that the strain is linearly related to the composition change [22].

Eq. (3) was first applied to metal systems by Larché and Cahn [20] and then was extended to nonlinear materials [23]. It was also applied to ionic solids containing charged defects in refs. [24,25]. The diffusion potential described in eq. (3) has a variety of applications. It can be used to determine the equilibrium concentration distribution of defects in solids with non-uniform stress field [26], and to study the stress caused by steady-state and transient diffusion in thin films and electrolytes by using the diffusion potential gradient as the driving force for diffusion [27,28]. The stress-dependent potential can also be used to simulate the kinetics demixing of solids under non-hydrostatic pressure [29]. It is worth noting that in addition to determining the diffusion equilibrium in solids, the chemical potential also controls the chemical equilibrium of solid state reactions [30]. The chemical reaction equilibrium constant is no longer just a function of temperature [31], but also a function of the stress state. Therefore, this is another level of coupling between the chemical reaction and the stress field. Finally, the boundary concentration also varies due to the applied boundary force and can be obtained by the stress-dependent diffusion potential in the boundary chemical reaction. Thus, the stress-dependent chemical potential couples the concentration field with the stress field.

Although the stress-dependent chemical potential described in eq. (3) has lots of applications, the differential equations that control diffusion and the mechanical equilibrium equations can be completely decoupled under certain conditions. The stress-dependent chemical potential described in eq. (3) is only a special case of a more general diffusion potential based on thermodynamics. Indeed, the Eshelby stress tensor should be the elastic contribution to the diffusion driving force, not the Cauchy stress [32]. That is why eq. (3) is only applicable under self-stress diffusion, i.e., the non-stoichiometry is the only source of stress.

4 Stress induced by oxide growth

When the metal materials are exposed to the high temperature oxygen-containing environments, oxidation reaction is highly prone to occurring so that oxide film forms. The stresses [33–36] and stress gradients [37,38] are generated in the dense oxide film, which in turn cause the buckling, cracking and even spalling of the oxide film. The measurements of the dimension change of the oxidized specimen [6,39], the strain by X-ray diffraction [40] and piezo-spectroscopic techniques [41] and the deflection of the oxidized specimen [42] directly prove the presence of stress in the oxide film. Although the stress in the oxide film has long been recognized, the mechanism of the stress origin during oxidation is still unclear. The earliest mechanism of stress origin in oxide films was proposed by Bedworth and Pilling [1]. They believed that the stress was caused by the volume difference between the oxide and the consumed metal. The volume ratio of the formed oxide to the consumed metal known as Pilling- Bedworth ratio (PBR) has the form of

$$\mathrm{PBR} = \frac{V_p}{N_m V_{\mathrm{met}}}, \tag{4}$$

where V_p, V_{met} and N_m are the molar volume of the oxide, the molar volume of the metal and the number of metal atoms in one unit oxide, respectively. For isotropic materials, the growth strain induced by PBR is

$$\varepsilon^{\mathrm{g}} = \sqrt[3]{\mathrm{PBR}} - 1. \tag{5}$$

When the PBR is not equal to 1, for example, greater than 1, stresses are generated in the constrained oxide layer and substrate. Thus, the region near the oxide-substrate interface in the oxide layer is subjected to compressive stress while the region near the oxide-substrate interface in the substrate is subjected to tensile stress. Huntz [43] emphasized that PBR is a key factor of stress generation in oxide layers with the preferential anion diffusion. The stress is smaller at the oxygen-oxide interface due to the weak geometric constraints while it is very large at the oxide-substrate interface [3]. The PBR of some common pure metals and alloys is listed in Table 1 [44]. The PBR theory can predict whether tensile stress or compressive stress is generated in a thick oxide film, but the calculated stress values are much larger than the experimental measurements, usually several orders of magnitude. In addition, the growth strain predicted by this theoretical model is only related to the molar volume of oxides and metals. The molar volume is independent of time, implying that the stress does not change with time.

Later, Rhines and Wolf [6] proposed a new model. In their model, the new oxide forms in the grain boundary perpendicular to the oxide-substrate interface in the oxide film, as shown in Figure 2. This leads to the lateral stress due to the lateral constraint of the substrate to the oxide film. On the contrary, the formation of the oxide lamella parallel to the oxide-substrate interface only increases the thickness of the oxide film without causing lateral stress. Figure 3 shows a schematic diagram of the possible formation position of the oxide lamella. There are three typical positions, i.e., the oxygen-oxide interface, the oxide film interior and the oxide-substrate interface. They correspond to the three situations that the cation diffusion rate is faster than the anion diffusion rate, the cation and anion diffusion rate are comparable, and the cation diffusion rate is slower than the anion diffusion rate, respectively. Rhines and Wolf's model has profound significance. Since then, many of the theoretical models are based on this model framework.

Table 1 PBR of some common metals and alloys [44]

Substrate	Oxide	PBR
K	K_2O	0.45
Mg	MgO	0.81
W	WO_3	3.30
V	V_2O_5	3.19
Cr	Cr_2O_3	2.07
Al	α-Al_2O_3	1.28
Al	γ-Al_2O_3	1.38
Ni	NiO	1.65
Ti	TiO_2	1.73
Ni-20Cr-0.4Ti	NiO	1.47
Ni-20Cr-0.4Ti	Cr_2O_3	2.14
Ni-30Cr-1.8Ti-1.0Al	Cr_2O_3	2.11
Fe-18Cr-9Ni-0.65Ti	Cr_2O_3	2.08
Fe-22Cr-5Al-0.3Y	Al_2O_3	1.92
Co-30Cr-6Al	Al_2O_3	1.94
Ti-5.0Al-2.5Sn	TiO_2	1.80

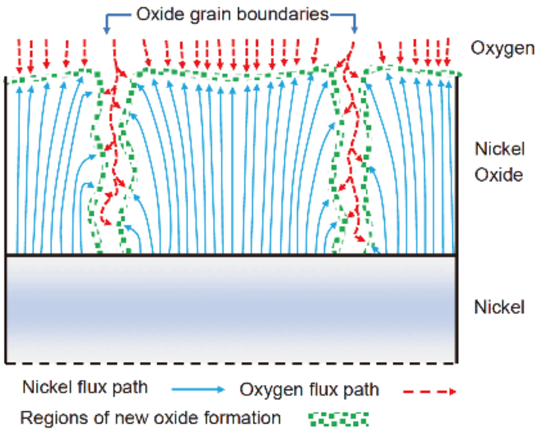

Figure 2 (Color online) Schematic diagram of diffusion path and newly formed oxide position, reproduced from ref. [6].

Speight and Harris [45] suggested that when the oxide forms at any position in the original oxide film, not necessarily at the grain boundary, compressive stresses are generated in the oxide film and tensile stresses in the substrate. And only a small amount of oxide generated in the oxide film will induce very large compressive stress. Evans [46] proposed that the oxide intrusion formed at the oxide-substrate interface acts as a linear center of dilatation, generating tensile stress in the substrate and compressive stress in the oxide. Based on the Rhines and Wolf's framework, an elastic analysis of stress in the oxide was carried out using the continuum dislocation theory [47]. Tolpygo et al. [48,49] experimentally measured the growth strain and found that the growth strain increased parabolically with the oxidation time. Based on the microstructure of the oxide layer and the assumption of rapid mixed diffusion at the grain boundary,

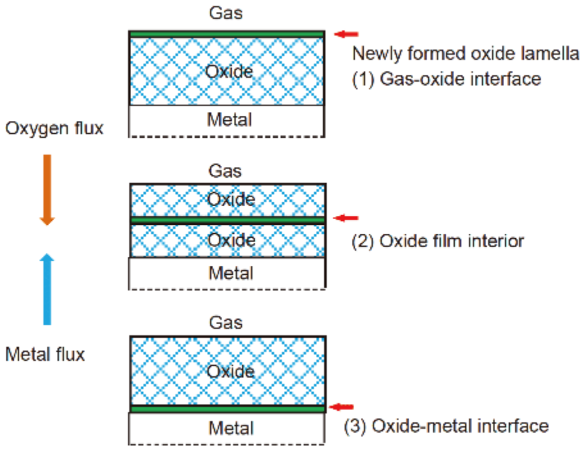

Figure 3 (Color online) Schematic diagram of possible position of the newly formed oxide lamella, reproduced from ref. [6].

Clarke [50] analyzed the origin of growth stress by using the dislocation climb model. A schematic diagram of the dislocation climb model is shown in Figure 4. The edge dislocations climb by trapping the “unlucky” counter-diffusing anions and cations at the dislocation cores. Most of the diffusing ions pass through the oxide film without being trapped. There are dislocations that climb inward from the oxygen-oxide interface and outward from the oxide-substrate interface. The climb of edge dislocations with Burgers vector perpendicular to the interface will produce lateral stress (for example, the A edge dislocation in Figure 4), while the climb of edge dislocations with Burgers vector parallel to the interface will not produce lateral stress (for example, the B edge dislocation in Figure 4). Through a series of derivations, Clarke gave the expression of the lateral growth strain rate $\mathrm{d}\varepsilon_g/\mathrm{d}t$ as

$$\frac{\mathrm{d}\varepsilon_g}{\mathrm{d}t}=D_{\mathrm{ox}}\frac{\mathrm{d}h_{\mathrm{ox}}}{\mathrm{d}t},\tag{6}$$

where D_{ox} and $\mathrm{d}h_{\mathrm{ox}}/\mathrm{d}t$ are the lateral growth coefficient and oxide film thickness change rate. From eq. (6), the growth strain rate is proportional to the growth rate of the oxide layer thickness. According to Clarke’s growth strain expression, the growth strain can be readily obtained as long as the growth kinetics of the oxide film is known, and then the stress in the oxide film can be calculated as well. The diffusion-controlled parabolic kinetics presented by Wagner [10] is often adopted.

Based on the Clarke’s model, many analyses on the stress in the oxide layer have been carried out [51–61]. On the basis of thermodynamic explanation, multi-scale method and symmetry property, Panicaud et al. [62] proposed a new explanation for the proportional relation between growth strain and oxide layer thickness, and analyzed the stress evolution in oxide layer using viscoplastic model. For the one-side oxidation case, many studies have also been conducted on the bending deformation of the oxide-substrate system [53,54,57,63,64]. Figure 5 shows the schematic diagram of the bending deformation of the oxide-substrate system during the one-side oxidation process.

As mentioned above, the growth strain calculated by the PBR is much larger than the measured value. Some researchers [65–67] adopted the various anisotropic strains, verified in refs. [65,68], which makes the growth strain more reasonable. The PBR is defined as $(1+\varepsilon_1)^2(1+\varepsilon_3)$, where ε_1 and ε_3 are the lateral strain and the strain along the oxide thickness direction, respectively. Take the zirconium/zirconia system as an example, its corresponding PBR is 1.56 and the anisotropic strain tensor is [67]

$$\boldsymbol{\varepsilon}=\begin{pmatrix}0.005 & 0 & 0\\ 0 & 0.005 & 0\\ 0 & 0 & 0.54\end{pmatrix}.\tag{7}$$

Despite of extensive studies on the stress evolution in oxide layers, much attention was paid to the average stress in the oxide layer and the distribution of stress in the oxide layer was not unveiled. Maharjan et al. [53,57] analyzed the stress distribution caused by the bending deformation of the oxide-substrate system during the one-side oxidation process. However, due to the thin oxide layer, the strain variation

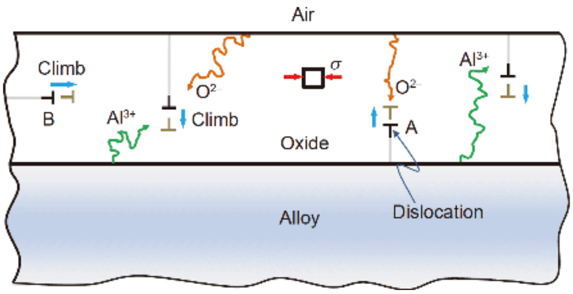

Figure 4 (Color online) Schematic diagram of the dislocation climb model, reproduced from ref. [50].

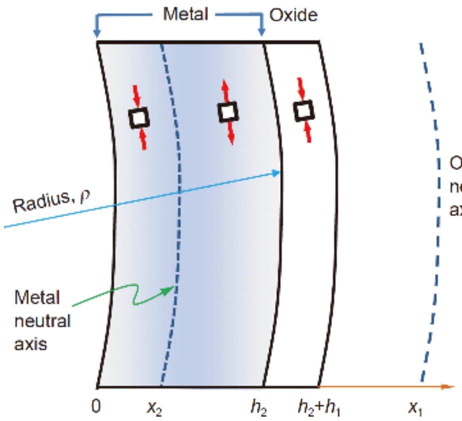

Figure 5 (Color online) Schematic diagram of bending deformation of oxide-substrate system during one-side oxidation process, reproduced from ref. [57].

along the oxide thickness direction caused by the bending deformation is very small, and so is the stress variation along the oxide thickness direction caused by the geometric deformation. Their calculated results show that the stress in the oxide layer is almost constant along the oxide thickness direction. The stress in the oxide layer changes slightly in the oxide thickness direction only when the oxide layer is very thick. In addition, Dong et al. [54] directly neglected the strain variation along the oxide thickness direction caused by the bending deformation, and assumed that the strain in the oxide layer did not change along the oxide thickness direction.

The Clarke's model can only predict the average stress in the oxide layer. In addition, the stress variation along the oxide thickness direction caused by the bending deformation can also be neglected. Therefore, the Clarke's model itself is incapable of predicting the stress distribution in the oxide layer. Besides, the articles reviewed in this section are only focused on the stress caused by the chemical reaction, but the influence of the stress generated in the oxide layer on the chemical reaction is not considered.

5 Interaction between stress and reaction

Chemical reactions could generate stress in the oxide layer. In fact, the stress also impacts the chemical reaction process. Zhang et al. [52] studied the effects of external loading on the oxidation kinetics and oxidation process, and pointed out that external tensile stress can promote the growth of oxide layers. Dong et al. [58,69] and Suo et al. [64] assumed that the stress in the oxide layer had an effect on the diffusion coefficient and analyzed the diffusion-stress coupling effect in the oxidation process. Their results revealed that the tensile stress may accelerate the oxidation rate while the compressive stress restrains the oxidation rate. Zhang et al. [52] introduced the effect of stress on the chemical reaction by the stress-dependent vacancy concentration, while such is introduced by the stress-dependent diffusion coefficient in Dong et al.'s [58,69] and Suo et al.'s [64] models. Qi et al. [70] experimentally studied the effect of tensile stress on the oxidation behavior of DZ125 Ni-based superalloy. The tensile stress leads to the formation of fast diffusion paths for Cr to diffuse to the surface. The initial oxidation rate is increased, but the less protective transient oxidation period is reduced by the rapid formation of protective chromic oxide layer. Overall, the oxidation resistance is improved.

In fact, there exists more direct coupling between stress and chemical reaction [71–74]. By the stress-dependent chemical potential, the stress can directly affect the diffusion of the reactants. At the same time, the strain energy is also incorporated into the chemical reaction affinity, and the stress can also directly affect the chemical reaction rate. Sallès-Desvignes [75] investigated the effect of stress on diffusion by both the stress-dependent diffusivity and the stress-dependent chemical potential. Yang et al. [76] modified the classical oxidation parabolic kinetics by introducing the stress effect on diffusion. Yue et al. [77] studied the stress-oxidation coupling effect by stress-dependent diffusivity and stress-dependent chemical reaction rate constant. Krishnamurthy et al. [78,79] and Zhou et al. [80–82] abandoned the Clarke's model. By treating the formed oxide as a new species, they gave the composition change strain. Using the elastic model, the stress distribution in the oxide layer was calculated. The mechanism of stress distribution here is due to the inhomogeneous distribution of the composition along the oxide thickness direction in the oxide layer. Even if the oxide layer is very thin, there still exists large stress gradient, which is quite different from the mechanism of stress distribution in refs. [53,57]. However, they only gave the elastic solution. For the stress relaxation mechanism in the oxide layer, such as plastic deformation and creep etc., Krishnamurthy et al. [78,79] and Zhou et al. [80–82] did not analyze. Loeffel and Anand [83] proposed a chemo-thermo-mechanically coupled theory accounting for elastic-visco-plastic deformation, diffusion and chemical reaction.

Based on the irreversible thermodynamics, Hu et al. [84] proposed the chemical Gibbs function variational principle, Helmholtz function variational principle and internal energy variational principle for the thermal-chemical-mechanical fully coupling problems. The evolving equations (or called the second constitutive equations) describing the interaction of the irreversible flows and irreversible forces were proposed as

$$\begin{aligned}
\mathrm{d}\boldsymbol{\eta}/\mathrm{d}t &= \mathbf{L}^{T}\cdot\mathbf{X}_{T}+\mathbf{L}_{N}^{T\mu}\cdot\mathbf{X}_{N}^{\mu}+\mathbf{L}_{r}^{TA}\cdot A_{r}+\mathbf{L}^{T\sigma}\cdot\boldsymbol{\sigma},\\
\mathrm{d}\boldsymbol{\xi}^{N}/\mathrm{d}t &= \mathbf{L}_{N}^{\mu T}\cdot\mathbf{X}_{T}+\mathbf{L}_{NM}^{\mu}\cdot\mathbf{X}_{M}^{\mu}+\mathbf{L}_{Nr}^{\mu A}\cdot A_{r}+\mathbf{L}_{N}^{\mu\sigma}\cdot\boldsymbol{\sigma},\\
\mathrm{d}w_{r}/\mathrm{d}t &= \mathbf{L}_{r}^{AT}\cdot\mathbf{X}_{T}+\mathbf{L}_{rN}^{A\mu}\cdot\mathbf{X}_{N}^{\mu}+\mathbf{L}_{rs}^{A}\cdot A_{s}+\mathbf{L}_{r}^{A\sigma}\cdot\boldsymbol{\sigma},\\
\mathrm{d}\boldsymbol{\varepsilon}^{(i)}/\mathrm{d}t &= \mathbf{L}^{\sigma T}\cdot\mathbf{X}_{T}+\mathbf{L}_{N}^{\sigma\mu}\cdot\mathbf{X}_{N}^{\mu}+\mathbf{L}_{r}^{\sigma A}\cdot A_{r}+\mathbf{L}^{\sigma}\cdot\boldsymbol{\sigma},
\end{aligned}\tag{8}$$

where $\mathrm{d}\boldsymbol{\eta}/\mathrm{d}t$, $\mathrm{d}\boldsymbol{\xi}^{N}/\mathrm{d}t$, $\mathrm{d}w_{r}/\mathrm{d}t$ and $\mathrm{d}\boldsymbol{\varepsilon}^{(i)}/\mathrm{d}t$ are the entropy flow vector, diffusion mass flow vector of the species N, rth reaction rate and irreversible strain, respectively. $\mathbf{X}_{T}$, $\mathbf{X}_{N}^{\mu}$, A_{r} and $\boldsymbol{\sigma}$ are the negative temperature gradient, negative chemical potential gradient of the species N, affinity of the rth reaction and stress. Due to the Onsager reciprocal relations, the coupling coefficients satisfy

$$\begin{aligned}
&\mathbf{L}_{N}^{T\mu}=\mathbf{L}_{N}^{\mu T},\ \mathbf{L}_{r}^{TA}=\mathbf{L}_{r}^{AT},\ \mathbf{L}^{T\sigma}=\mathbf{L}^{\sigma T},\ \mathbf{L}_{NM}^{\mu}=\mathbf{L}_{MN}^{\mu},\\
&\mathbf{L}_{Nr}^{\mu A}=\mathbf{L}_{rN}^{A\mu},\ \mathbf{L}_{N}^{\mu\sigma}=\mathbf{L}_{N}^{\sigma\mu},\ \mathbf{L}_{rs}^{A}=\mathbf{L}_{sr}^{A},\ \mathbf{L}_{r}^{A\sigma}=\mathbf{L}_{r}^{\sigma A}.
\end{aligned}\tag{9}$$

If the coupling effects are not considered, the first and second equations of eq. (8) can be reduced to Fourier law and Fick law, respectively. The third equation is the chemical reaction rate containing the influence of stress on the reaction, which was verified by Craig [85]. The last equation is the irreversible strain including the growth strain and creep strain, etc. Eq. (8) has been successfully applied in the study of the interfacial reactions between γ-TiAl alloy and glass-ceramic coating [86]. In addition, Yu et al. [87] further took the electrical effect into account and proposed a thermo-mechano-electro-chemical fully coupling theory.

Suo et al. [88] proposed a modified growth strain formula based the evolving equations as

$$\frac{\mathrm{d}\varepsilon_{\mathrm{ox}}^{g}}{\mathrm{d}t} = a\sigma + D_{\mathrm{ox}}\frac{\mathrm{d}h_{\mathrm{ox}}}{\mathrm{d}t}, \tag{10}$$

where a is the proportional coefficient, D_{ox} and h_{ox} are the lateral growth coefficient and oxide thickness, respectively. The modified growth strain includes the effect of stress on it. If the effect of stress on the growth strain is neglected, eq. (10) is reduced to the Clarke's model [50].

Based on the evolving equation, Wang et al. [89,90] derived the location-dependent growth strain and analyzed the mechanics-diffusion-chemical fully coupling effect in inelastic and viscoplastic oxide layer during oxidation process. Since the growth strain is location-dependent, the stress is naturally location-dependent. The stress distribution with viscoplastic model is shown in Figure 6. It can be seen that the stress distribution in short oxidation time is quite different from that in long oxidation time. In short oxidation time, the stress in the oxide scale is dominated by the growth strain. The stress is maximum at the oxide-substrate interface, and then decreases gradually along the oxide thickness direction. At the oxygen-oxide interface, the stress reaches the minimum value. In long oxidation time, the stress distribution is the competition result of growth strain and viscoplastic strain.

The theory hinted by eq. (8) fully couples diffusion-thermo-chemo-mechanical effects. Such theory may find wide applications in revealing the comprehensive properties of materials in the complex service conditions. However, the analytical solution of problems described by eq. (8) is usually impossible. To obtain the numerical solutions may resort to the finite element method [86]. Such can be more easily achieved by incorporating the fully coupled theory into the commercial software such as ABAQUS [91,92].

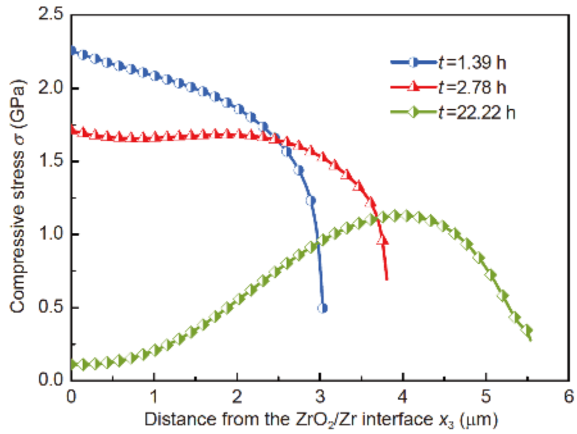

Figure 6 (Color online) Stress distribution in the viscoplastic oxide layer, reproduced from ref. [90].

6 Conclusions

This paper mainly reviews the chemo-mechanical coupling effects in the oxidation of metal materials. The coupling effects during the oxidation can be summarized as follows:

(1) Effect of chemical reaction on the stress field by the growth strain;

(2) Effect of chemical reaction on the diffusion by altering the diffusing species concentration;

(3) Effect of stress on chemical reaction by changing the chemical reaction rate;

(4) Effect of stress on diffusion in two aspects, i.e., stress-dependent diffusion coefficient (thermodynamics effect) and stress-dependent chemical potential (kinetics effect);

(5) Effect of diffusion on chemical reaction by altering the reactants concentration;

(6) Effect of diffusion on stress by chemical expansion strain.

The intrinsic origin of stress (not caused by geometry) in the oxide layer mainly includes:

(1) Various anisotropic-strain derived from PBR;

(2) Growth strain predicted by Clarke's model;

(3) Composition change strain by treating freshly formed oxide as a new species;

(4) Location-dependent growth strain derived from evolving equations (fully coupled model).

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