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Theoretical aspects of oxidation of composite materials

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Abstract. — Relationships between the high-temperature oxidation behavior and the composite architecture (shape, size, volume fraction, and orientation of the reinforcement phase) are proposed.

1. Introduction.

Composite materials represent a new generation of high-temperature structural materials. The importance of composite materials is reflected in the significant amount of research effort that has been expended in recent years to characterize their mechanical properties. Interestingly, however, research directly aimed at the high-temperature environmental durability of composite materials has been scarce. For example, El Dahshan *et al.* [1] oxidized Ni-20Cr containing W fibers, Park and Simkovich [2] oxidized Fe-Cr alloys containing Si_3N_4 particles, Wagner and Simkovich [3] oxidized Co-Cr alloys containing Si_3N_4 particles, Lin *et al.* [4] oxidized Al_2O_3 -SiC whisker composites, Korinko *et al.* [5] oxidized NiAl/TiB₂ composites, and Fish and Duquette [6] oxidized a TiAl/ Al_2O_3 whisker composite. In addition to limited experimental studies, little theoretical work has been done to establish a proper foundation for understanding the high-temperature oxidation behavior of composite materials. Qualitative treatments of the oxidation behavior of multiphase materials have been given by Stringer *et al.* [7] and Bastow *et al.* [8]. Semi-quantitative treatments of the oxidation behavior of binary alloys have been presented by Wahl [9], and Wang *et al.* [10].

The purpose of this paper is to analyze both the possible stability diagrams and the oxidation kinetics involved in the high-temperature oxidation of a composite structure. In particular, the diffusional flux in the matrix phase to support the exclusive formation of a protective scale are related to the architecture of the composite (i.e. shape, size, volume fraction, and orientation of the reinforcements).

2. Thermodynamics.

The oxidation tendency of a material is greatly dependent on the thermodynamics of the reaction. In most cases, this reaction tendency can be presented graphically at a given temperature as a function of the material composition and oxygen activity. Such a thermodynamic representation is called a "stability diagram" in the oxidation community, and has been widely used in analyzing the oxidation behavior of various monolithic materials, especially binary alloys, and more recently for intermetallic compounds [11].

The construction of a stability diagram for a composite material, offers two major challenges. First, a composite material is generally a multicomponent system, so that a two-dimensional graphic representation can hardly describe the entire system. Second, a composite material is a multiphase system, which includes not only a matrix phase and a reinforcement phase but in some cases also one or more interfacial intermediate phase(s) between the matrix and the reinforcement phase. Furthermore, the entire composite system may not be at thermodynamic equilibrium, so that some serious interfacial reactions between the matrix and the reinforcement phase may occur in addition to surface oxidation at the service temperatures. In the following analysis, the composite material is simplified to a model system which can be more readily analyzed based on our understanding on alloy oxidation.

Let us consider a simple two-phase system containing a matrix phase M and a reinforcement phase R with no stable intermediate phase between them. The matrix phase contains primarily component A with a very limited solubility for component B; likewise, the reinforcement phase contains primarily component B with a very limited solubility for component A. Assume that the component B forms a more stable oxide BO than oxide AO (the oxide stoichiometries are conveniently assumed to be AO and BO). There are two possible kinds of stability diagrams for such a simple composite. In the stability diagram shown in figure 1, oxides AO and BO form a continuous solid solution. In the stability diagram shown in figure 2, a very limited solubility for the other component is permitted for each oxide. Again, no stable intermediate oxide compound forms.

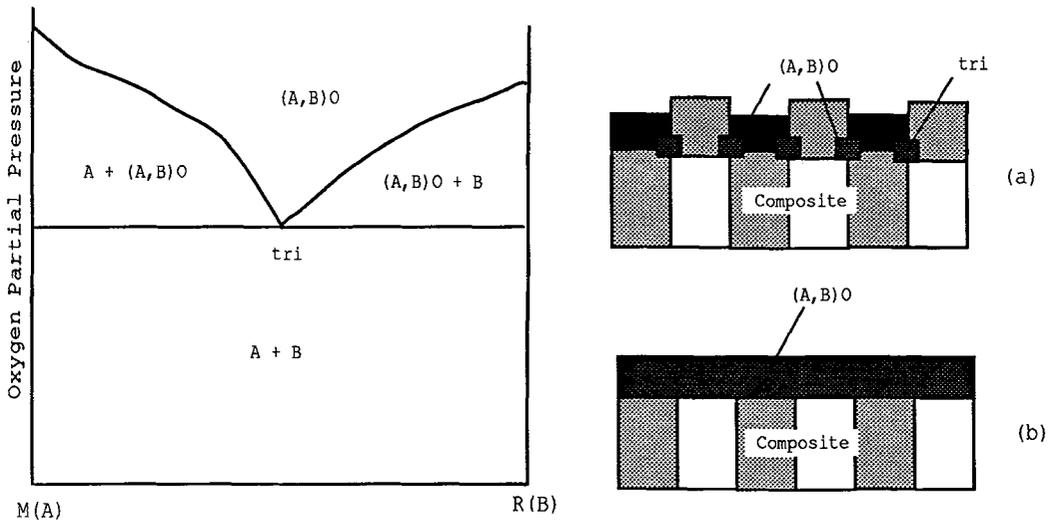


Fig. 1. — Stability diagram of a composite system forming a solid solution oxide, and possible oxide scale morphologies, where M is the A-rich matrix phase and R is the B-rich reinforcement phase: a) morphology developed at an early stage; b) morphology developed at a later stage.

In figure 1, oxides AO and BO form initially on the matrix and the reinforcement phases, respectively, but at the triple point (tri, see Fig. 1a), AO and BO react to form the solid solution $(A,B)O$. This solid solution keeps growing and eventually covers the entire surface of the composite (see Fig. 1b) as indicated by the stability diagram. If one of the oxides (either

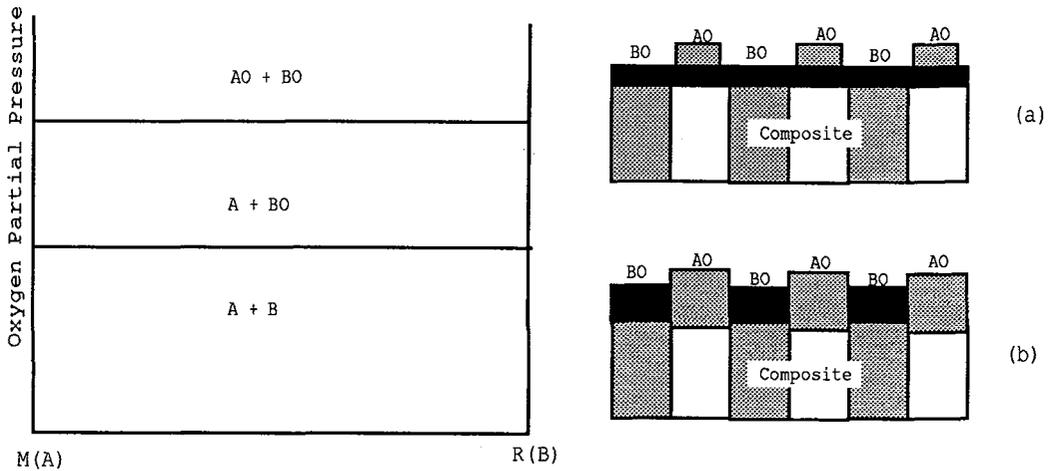


Fig. 2. — Stability diagram of a composite system forming two nearly-insoluble oxides, and possible oxide scale morphologies: a) protective oxide forms to slow down further oxidation; b) two phases oxidize independently.

AO or BO) has poor oxidation resistance, it is unlikely that the solid solution oxide will be protective, since the defect structure from the less-resistant oxide will be inherited by the solid solution.

In figure 2, the most stable oxide BO forms initially on both the matrix phase and the reinforcement phase. Stringer *et al.* [7] have pointed out that the same oxide should form on both phases of a two-phase alloy, since at equilibrium the two alloy phases should have identical chemical activities for each component. If BO is highly oxidation-resistant, AO will either not form or stop growing.

Otherwise, A may readily diffuse through the non-protective BO to form an AO layer on top of the BO (see Fig. 2a), as often observed in alloy oxidation. However, in some other situation, an independent oxidation for each phase may be observed, i.e. AO forms primarily on phase M (A-rich) and BO forms primarily on phase R (B-rich) as shown in figure 2b. Whether a protective BO forms on both phases or AO and BO form on each phase independently is largely a consequence of kinetic factors, which will be discussed in the following sections.

3. Kinetics.

The oxidation of a single phase alloy may lead to either a mixed oxide scale on the surface or the exclusive formation of the most stable oxide of the alloy constituents, which in most cases is a slow-growing protective oxide scale. Wagner [12] established a criterion for the exclusive formation of the protective scale on a binary single-phase alloy by balancing the supply of the more reactive constituent migrating from the bulk of the alloy to the alloy/scale interface and the consumption of this constituent at the alloy/scale interface to form its scale. The critical concentration of the alloy constituent necessary for the enhanced oxidation resistance in a single phase alloy is commonly known as the Wagner's criterion for the exclusive formation of a protective scale.

When a composite material is exposed to an oxidizing environment, each phase in the

composite will oxidize at different scaling kinetics, but Wagner's criterion may be applied to each phase separately. If Wagner's criterion for the exclusive formation of a particular oxide is satisfied for each of the phases, then a continuous layer of this oxide may form exclusively on the composite. Otherwise, if Wagner's criterion is satisfied for only one of the two phases, each phase may oxidize in a different manner; e.g., the reinforcement phase may oxidize slowly due to the formation of the protective oxide while a fast-growing oxide may form on the matrix phase, or *vice-versa*. However, there are some cases where Wagner's criterion is not satisfied for one of the two phases, yet a given protective scale forms on the entire material [13]. As discussed later, this can be attributed to the interaction between the diffusion fields from each phase, and there are three possible situations.

3.1 NO INTERACTION BETWEEN THE MATRIX PHASES AND THE REINFORCEMENT PHASE. — In this case, the diffusion fields of the two phases in the composite are not overlapping, so that the two phases oxidize independently. Additive oxidation kinetics can be applied to this situation, which introduces another "law of mixtures" for composite materials. If both oxides obey the parabolic-growth laws, the global kinetics will also be parabolic, and the following relation exists between the parabolic constants:

$$\sqrt{k_{\text{total}}} = \phi_M \sqrt{k_M} + \phi_R \sqrt{k_R} \quad (1)$$

where the k_{total} , k_M , and k_R are the parabolic rate constants for scale growth on the composite, the matrix phase, and the reinforcement phase, respectively; ϕ_M and ϕ_R are the volume fractions of each phase. Knowing that $\phi_M + \phi_R = 1$, and substituting this into equation (1), the overall parabolic rate constant for the composite material can be restated as:

$$\frac{k_{\text{total}}}{k_M} = \left(\sqrt{\frac{k_R}{k_M}} - 1 \right)^2 \phi_R^2 + 2 \left(\sqrt{\frac{k_R}{k_M}} - 1 \right) \phi_R + 1 \quad (2)$$

This relation can be regarded as the "law of mixtures" for the oxidation of composite materials when there is no interaction between the two phases; this relation is shown in figure 3. Logarithmic values of the k_{total} -to- k_M ratio are presented in this figure for a clear illustration. As indicated in figure 3, a higher k_R -to- k_M ratio gives rise a higher global rate constant with increasing the volume fraction of the reinforcement phase, whereas a lower k_R -to- k_M ratio offers a reduced total oxidation rate constant with increasing the volume fraction of R. The apparent activation energy of the overall rate constant is also a combination of the activation energies for each phase.

$$Q_{\text{total}} = \phi_M \sqrt{\frac{k_M}{k_{\text{total}}}} Q_M + \phi_R \sqrt{\frac{k_M}{k_{\text{total}}}} Q_R \quad (3)$$

where Q 's are the activation energies. It can be noted that this "law of mixtures" for activation energies is slightly different from the one proposed for a multilayered-oxide scale by Gleeson *et al.* [14].

3.2 STRONG INTERACTION BETWEEN THE MATRIX PHASE AND THE REINFORCEMENT PHASE. — In this case, the diffusion fields from the two phases overlap considerably. A denuded zone can be found near the surface, where the reinforcement phase quickly dissolves into the

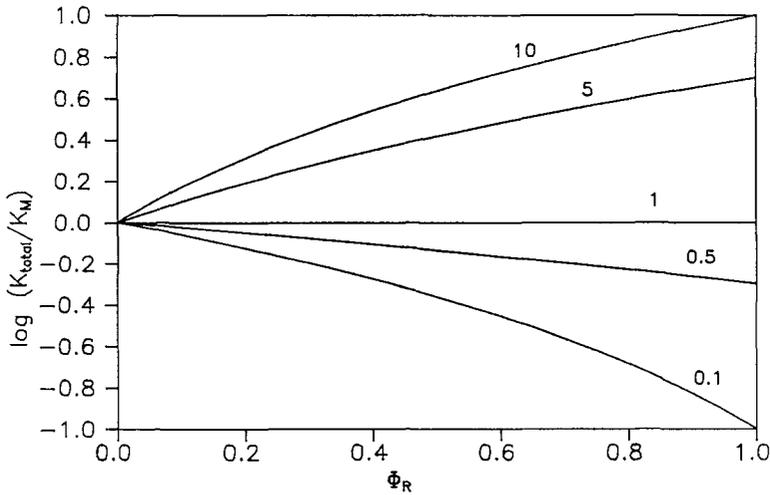


Fig. 3. — Additive oxidation kinetics, where k_{total} is the parabolic rate constant for overall composite, k_M for matrix phase, and k_R for reinforcement. ϕ_R is the volume fraction of the reinforcement. The values in the figure indicate the k_R -to- k_M ratios in the composite.

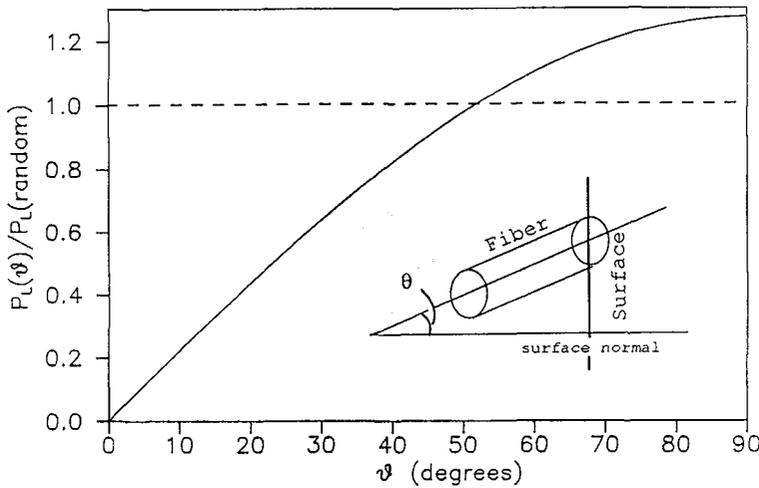


Fig. 4. — $P_L(\theta)$ as a function of the orientation between the fiber and the surface. The angle θ is defined between the fiber orientation and the surface normal. $P_L(\text{random})$ is the P_L for random fiber orientation.

matrix phase to support a selective removal of one of the components at the oxidizing surface. Wahl [9] developed an analysis for a two-phase structure where a near-surface denuded zone develops by a quick dissolution of the second phase; this analysis can be readily applied to a composite structure where the rapid dissolution of the reinforcement phase occurs beneath the surface. By Wahl's criterion, the exclusive formation of the most stable and slow-growing

oxide scale BO can be achieved, only if the following condition is met:

$$\sqrt{N_B^0 N_B^{\text{tot}}} > \frac{V}{V(\text{BO})} \sqrt{\frac{\pi k_p}{2D}} = N_B^W \quad (4)$$

where N_B^0 and N_B^{tot} are the mole fractions of component B in the matrix phase and in the overall composite, respectively, V and $V(\text{BO})$ are the molar volumes of the composite material and of the oxide BO, respectively, k_p is the parabolic rate constant for the growth of oxide BO, D is the interdiffusion coefficient for the matrix phase, and N_B^W is the Wagner's critical concentration for the exclusive formation of oxide BO on the matrix phase. Wahl treated this two-phase system by a steady-state diffusion model with no consideration given for the architecture of the microstructure, i.e. the shape, size, and orientation of the second phase.

3.3 LESS STRONG INTERACTION BETWEEN THE MATRIX PHASE AND THE REINFORCEMENT PHASE.

— In most situations, a total dissolution of the reinforcement phase near the surface does not necessarily occur; however, the exclusive formation of the slow-growing oxide BO is still possible. A non-steady state diffusion analysis for a two-phase structure has been provided by Wang *et al.* [10]. In their analysis, an average diffusion flux from the two-phase structure to the surface was evaluated by considering the unidirectional diffusion in multiple diffusion columns, and the length of each column was related to the microstructure of the two-phase structure. Their analysis was able to relate the oxidation behavior of the two phase structure to the architecture of its second phase. The criterion for the exclusive formation of the protective oxide BO scale was found to be:

$$P_L \sqrt{Dt} > \Phi \left(\frac{N_B^0}{N_B^W} \right) \quad (5)$$

where P_L is a microstructural parameter defined in quantitative metallography, which is used here to describe the number of intercepts per unit length of the interphase boundary by a linear probe. Further D is the interdiffusion coefficient of the matrix phase, t is time, N_B^0 is the solubility of B in the matrix phase, and again N_B^W is Wagner's critical concentration for the matrix. The function $\Phi(\)$ is a monotonically-decreasing function given in reference (10). The P_L can further be related to the volume fraction (ϕ_R), the size, and the geometries of the reinforcement phase. For example, for a spherical phase with a radius r , $P_L = \frac{3\phi_R}{2r}$;

for a cubic phase with an edge length a , $P_L = \frac{3\phi_R}{a}$; for a cylindrical phase with a radius r

and length l , $P_L = \frac{l+r}{lr} \phi_R$. As can be seen from these relationships, a preferred composite architecture for a good oxidation resistance requires a higher P_L as well as a higher N_B^0 , which in turn requires a greater volume fraction and smaller dimensions of the second phase.

Generally, a fine, dense, and homogeneously-distributed reinforcement phase which is rich in the component forming a stable, slow-growing oxide should perform better than some other reinforcement incorporated otherwise into the matrix.

The orientation of the reinforcement phase in a composite material represents another important aspect of its architecture. According to quantitative metallography, $P_L = \frac{2}{\pi} L_A$, where L_A is another parameter in metallography called line length per unit area. By utilizing this relationship, it can then be shown that for a composite containing continuous straight

fibers with a θ angle between the fiber orientation and the surface normal (shown in Fig. 4), the $P_L(\theta)$ -to- P_L (random) ratio is

$$\frac{P_L(\theta)}{P_L(\text{random})} = \frac{4}{\pi} \sin(\theta) \quad (6)$$

where $P_L(\theta)$ is measured along the given θ direction, and $P_L(\text{random})$ is for a randomly-oriented fiber architecture. As shown in figure 4, for a surface with a θ value greater than about 52° (fiber is nearly parallel to the surface), the configuration offers an enhanced oxidation protection over the random configuration, whereas for a surface with the orientation less than about 52° with respect to the fiber direction (fiber is nearly perpendicular to the surface), the configuration yields a worse oxidation protection than the random configuration. This effect was observed by Stott *et al.* [15] in the oxidation of a directionally-solidified two-phase eutectic structure.

4. Concluding remarks.

The oxidation behavior of composite materials involves both the thermodynamics and diffusion kinetics. For a system which forms a solid solution oxide, an enhanced oxidation resistance in the composite material is unlikely. However, real systems exhibit more often the formation of a mixed-oxide compound (e.g. spinel) than the formation of a continuous solid solution. For the exclusive formation of a slow-growing protective oxide scale on a composite, not only is a sufficient solute solubility in the matrix required, but also a sufficient amount of solute-rich second phase is needed. Certain second-phase geometries and distributions are more desirable than the others, and a fiber orientation perpendicular to the oxidizing surface is not preferred. The value of $P_L\sqrt{Dt}$ represents an important parameter in a multiphase structure, which in fact describes the ratio between the solute-diffusion length in the matrix (\sqrt{Dt}) and the average interval between the matrix/reinforcement boundaries (a parameter proportional to P_L^{-1}). For a system where the diffusion length is too small when compared to the average-interphase-boundary interval, the two phases oxidize independently, and an additive relationship can be applied to the overall kinetics. For a system with strong interaction between the matrix and the reinforcement (i.e. a significant diffusion length in the matrix), a dissolution approximation (Wahl's treatment) may be adequate. However, for some composites, where the solute diffusion length in the matrix is comparable to the dimensions of the average-interphase-boundary interval, the relation between the oxidation behavior and the architecture of the composite material is more complex.

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