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Theoretical consideration on composite oxide scales and coatings

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Abstract: The present paper discussed some fundamental aspects on composite oxide scales and coatings for protection of alloys from high temperature oxidation, the related thermodynamic conditions, special mechanical characteristics and a sealing mechanism. It was proposed that the oxide scales and coatings with a composite structure should possess superior mechanical properties than that with a single phase oxide. It also showed that the Al_2O_3 scales or coatings doped with Y_2O_3 and ZrO_2 (or YSZ)-Al_2O_3 composite coatings possessed superior properties at high temperatures. In such composite oxide scales and coatings, the fracture resistance of the scales was increased by the toughening effect, the thermal stress was decreased owing to the increase of thermal-expansion coefficients, and Al_2O_3 phase could seal the alloy substrate well. In addition, the kinetic equation of thermal growth oxide on alloy covered with composite oxide coatings was derived.

Keywords: rare earth oxides; composite oxide scales; composite oxide coatings; high-temperature oxidation of alloys

It is well known that the oxidation resistance of alloy coatings is determined by the formation of Al_2O_3, Cr_2O_3 or SiO_2 scales and their failures caused by the stresses generated in oxide scales. The stresses mainly consist of growth and thermal stresses, due to which oxide scale cracking and spallation take place. With ceramic coatings, the oxidation resistance of alloys mainly depends on the integrality of ceramic coatings. Therefore, the processes of scale cracking and spalling are the key factor to influence the lifetime of alloy and ceramic coatings.

A number of models on the processes of cracking and spalling of oxide scales have been proposed so far. These models normally assume that the oxide scale formed on alloys is a homogeneous single phase material[1,2]. Consequently, cracking and spalling of oxide scales and ceramic coatings with a single phase cannot be avoided completely.

As ceramic composites can effectively enhance the strength and durability of ceramic components and improve their fracture toughness, it is reasonable to propose that the oxide scales and coatings with a composite structure should possess improved mechanical properties than that with a single phase oxide. In fact, the most of oxide scales formed on alloys are composites. For example, $NiO/NiCr_2O_4$ and $NiO/NiAl_2O_4$ muti-layered scales can form on Ni-Cr and Ni-Al alloys; Al_2O_3 and Cr_2O_3 scales doped with small amount of rare earth oxides can be formed on Ni-Cr-Al-RE and Ni-Cr-RE (RE denotes rear earth elements) alloys[3]. These composite oxide scales often exhibit better resistance to cracking and spallation than the single phase oxide scale. In addition, recent researches have shown that the ceramic coatings with composite structures can effectively resist scale spallation and oxidation at high temperature[4,5].

In this paper, theoretical consideration on the composite oxide scales and coatings will be presented by taking Y_2O_3 doped Al_2O_3 scales and ZrO_2-Al_2O_3 or YSZ (yttrium stabilized zirconia)-Al_2O_3 composite coatings as examples.

1 Fundamental aspects on composite oxide scales and coatings

1.1 Thermodynamic condition

By the definition, composite oxide scales and coatings should have a multi-phase structure. Therefore, the ingredients of composite oxide scales and coatings should be located in a eutectic zone of phase diagrams, such as Al_2O_3-Y_2O_3[6], ZrO_2-Al_2O_3[7] phases diagrams. By this way, composite oxide scales and coatings with various structure design for improving both mechanical properties and oxidation resistance must be thermodynamically stable. As shown in Fig. 1, the eutectic zones in the phase diagrams of binary metal oxides used for designing composite oxide scales and coatings can be divided into three types: (1) $metal_a$ oxide–$metal_b$ oxide eutectic zone; (2) $metal_a$ oxide–$metal_a$+$metal_b$ oxide compound (including solid solution) eutectic zone; and (3) $metal_a$+

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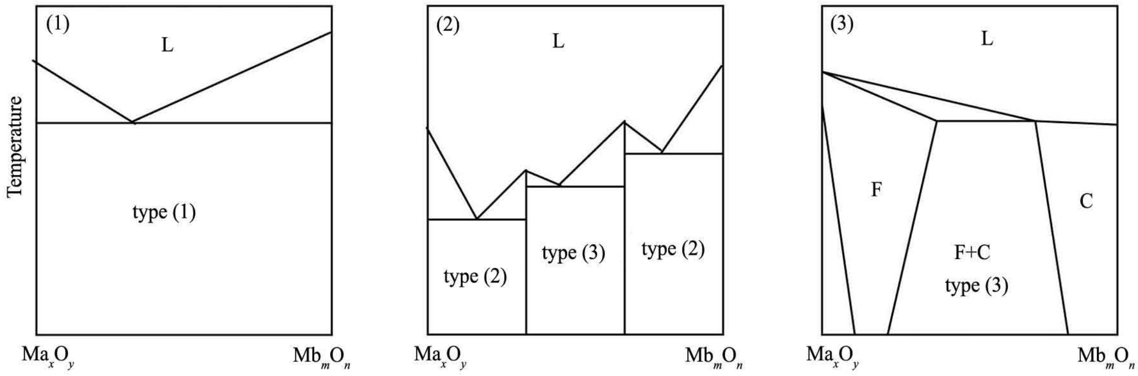

Fig. 1 Three types of eutectic zones in phase diagrams of binary metal oxides

$metal_b$ oxide compound (α)–$metal_a$+$metal_b$ oxide compound (β) eutectic zone.

1.2 Special mechanical properties

The mechanical properties of ceramics including strength, fracture toughness and plasticity can be effectively improved by the formation of multi-phase composite. According to the types of reinforcements, the toughening effects of composite ceramics can be divided into nano-particle toughening, micro-particle toughening, whisker toughening, fiber toughening and multilayer toughening. The main toughening mechanisms in multi-phase composite ceramics include phase transformation toughening, microcrack formation, crack deflection, crack bridging, etc., as shown in Fig. 2.

It is reasonable to propose that above mechanisms can be used to explain the behavior of composite oxide scales and coatings. However, because the real materials studied for high temperature oxidation involve composite oxide scales, coatings and alloys substrate, the stresses generated in composite oxide scales or coatings are restricted by the alloy substrates as the oxidation progresses. The mechanical behavior in composite oxide scales or coatings is more complicated than that in bulk composite ceramics. Moreover, owing to the limitation in thickness, composite oxide scales or coatings are often designed and fabricated to possess finer structures than that of the bulck composite ceramics. Therefore, it is necessary to study the special mechanical characteristics in composite oxide scales or coatings.

Cracking and spalling of oxide scales and coatings are often caused by thermal stresses, which arise from differential thermal expansion between the alloy substrate and scale. Timoshenko[8], derived the thermal stress, σ_{ox}, in oxide scale during cooling as:

$$\sigma_{ox} = \frac{-E_{ox}(\alpha_{ox} - \alpha_m)\Delta T}{1-v} \quad (1)$$

Where E_{ox} is the elastic modulus, α_{ox} and α_m are the linear thermal-expansion coefficients for the oxide and metal, and ΔT is the change in temperature. As analyzed by Evans et al.[9,10], spallation of a single phase oxide scale will occur when the elastic strain energy stored in the scale exceeds the fracture resistance, G_c, of the interface. The criterion for failure is given as the following equation:

$$(1-v)\sigma_{ox}{}^2 h / E_{ox} > G_c \quad (2)$$

Where v is the Poisson's ratio of the oxide scale, h is the scale thickness, and σ_{ox} is the equal biaxial residual stress in the scale.

Comparing with the single phase oxide scales and coatings, the fracture resistance, G_c, of composite oxide scales or coatings can be enhanced by toughening actions. According to Eq. (2), there are two conditions to avoid scale spallation: increasing G_c that permits the oxide scale to withstand bigger stresses, or decreasing the stress, σ_{ox}, in oxide scales by increasing the thermal-expansion coefficients, α_{ox}, in Eq. (1).

1.3 Sealing mechanism

In order to improve the oxidation resistance of an alloy, we propose a "sealing mechanism" for designing the composite oxide scales or coatings. Such oxide scales or coatings should have a special structure, in which at least

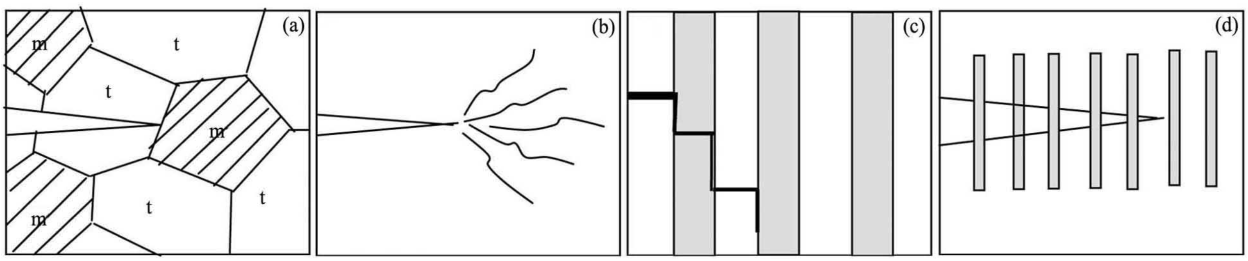

Fig. 2 Toughening mechanisms in multi-phase composite ceramics
(a) Phase transformation toughening; (b) Microcrack formation; (c) Crack deflection; (d) Drack bridging