Chapter 7
Nanocrystalline, Enamel and Composite Coatings for Superalloys

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ABSTRACT
This chapter describes several innovations for improving the performance of high-temperature coatings. Nanocrystallization has been demonstrated to be a practical way to prolong the lifetime of high temperature coatings by decreasing the minimum Al concentration for sustaining the growth of thermally grown oxide (TGO) scales, and increasing the resistance against scale cracks and spallation. Enamel coatings with enhanced strength, toughness and thermophysical properties were developed for improving the hot corrosion resistance of superalloys. Low expansion nanocomposite coatings minimize the mismatch between coefficients of thermal expansion (CTEs) of the TGO scales and the underlying coatings, so allow growth of thicker TGO scales free of cracks and spallation and then prolong the lifetime.

INTRODUCTION
The major driving force for the development of high temperature protective coatings is the demand for advanced gas turbines with improved fuel efficiency and reduced carbon emissions, which may be achieved by raising the turbine inlet temperatures. For example, the turbine inlet temperatures of M501G and M501J (Mitsubishi Heavy Industries Ltd.) are 1500 °C and 1600 °C, while their combined-cycle efficiencies (gross, low heat value, ISO base) are ≥58% and ≥61.5%, respectively.

Earlier development of heat-resistant alloys was burdened by both oxidation resistance and mechanical properties at high temperatures. There are conflicts in chemical compositions, however, for simultaneously optimizing the oxidation resistance and the mechanical properties. For example, higher concentration of refractory elements, e.g. Mo, W, and Ta, is beneficial to longer high temperature creep-rapture lifetime.
of an alloy while is detrimental to the oxidation resistance. The idea of developing protective coating technology releases half of the burdens, i.e. oxidation resistance, at least partially. By applying protective coatings on the surface of components, one can focus his goal on pursuing longer creep-rapture lifetimes by adding more refractory elements into his alloys while leave the task of optimizing the oxidation resistance to others who work on the development of the protective coatings.

Several protective coatings, i.e. diffusion coatings, overlay coatings and thermal barrier coatings (TBC) have been widely used in advanced gas turbines up to date. Diffusion coatings are mainly Cr-rich coatings, simple aluminide coatings and platinum modified aluminide (NiPtAl) coatings. Overlay coatings typically comprise β+γ' in γ matrix and are of composition MCrAlY (M is Ni, Co, or NiCo). TBC consists of a bondcoat, which is either an overlay coating or a diffusion coating, and a topcoat, which is a ceramic thermal insulator, e.g. yttria-stabilized zirconia (YSZ). In this chapter, the main achievement and the intrinsic issues of the above-mentioned traditional coatings will be briefly reviewed, and then several novel coatings will be introduced in purpose of exploring new pathways of protective technology for high temperature applications. The first one is the nanocrystalline coatings, which aim at improving the performance of coatings by nano-sized grain effects that decrease the minimum Al concentration for sustaining the growth of thermally grown oxide (TGO) scales and increase the resistance against cracks and spallation of TGO. The second one is the enamel coatings, which have quite low oxygen permeation rates and solubility in molten sulphates. The primary purpose of studying enamel coatings is to develop a coating that has hot corrosion rates same as oxidation rates, because the hot corrosion rates of the traditional coatings are much higher than their oxidation rates. The third one is low expansion nanocomposite coatings, which minimize the mismatch between the coefficients of thermal expansion (CTEs) of the TGO scales and the underlying coatings and thus allow growth of thicker TGO scales free of cracks and spallation than those on metallic coatings.

BACKGROUND

Theoretical Lifetimes of Protective Coatings

High temperature protective coatings are mainly based on aluminide, because the TGO formed on aluminide is slowly-growing α-Al₂O₃. The coating failure may be referred to as breakdown oxidation where the oxidation rates are dramatically accelerated because the growth of α-Al₂O₃ is replaced by less protective TGO due to insufficient Al supplies.

The growth of a protective α-Al₂O₃ scale is expressed by parabolic law:

\[
(\Delta w)^2 = k_p t
\]  

(1)

where Δw is the mass gain per unit area, \(k_p\) the parabolic constant, and \(t\) the tested time. The scale thickness, \(h\), can be calculated by

\[
h = \frac{\Delta w}{(1 - \beta) \gamma}
\]  

(2)
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