Performance of CVD Al₂O₃ Intermediate Layer between Zirconia Top Coat and NiCrAlY Bond Coat

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An attempt to apply CVD Al₂O₃ coating as an intermediate layer to ZrO₂-8 mass% Y₂O₃/Ni-22Cr-10Al-1Y thermal barrier coatings (TBCs) for protecting the Ni-22Cr-10Al-1Y bond coat from oxidation during cyclic operations was evaluated in this study. Results of this study showed that the intermediate CVD Al₂O₃ layer between the zirconia top coat and the Ni-22Cr-10Al-1Y bond coat can effectively reduce the oxidation rate of the bond coat and hence remarkably improve the performance of TBCs under thermal cycling tests at 1273 K. However, optimization of the CVD process parameters is needed to exclude the adverse effects induced by the application of CVD Al₂O₃ in the TBC systems; i.e., an increase in operationally induced stresses and premature failures resulting from undesirable Al₂O₃ morphologies. It was concluded that the thickness and microstructure of CVD Al₂O₃, which are affected by the processing parameters, are the main factors influencing the cyclic life of triplex ZrO₂-8 mass% Y₂O₃/CVD Al₂O₃/Ni-22Cr-10Al-1Y thermal barrier coatings.

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1. Introduction

Since the late 1970s, plasma spraying of thermal barrier coatings (TBCs) has been recognized as a feasible process to increase the operating temperature or durability of superalloys[5][6][7]. Traditional TBC systems provide thermal insulation to critical air cooled components by overlaying a strain tolerant zirconia top coat. An intermediate layer of MCrAlY (where M indicates Ni, Co, Fe, or their combinations) bond coat is sprayed before overlaying with the top coat to protect the superalloy substrates from high temperature oxidation and hot corrosion when exposed to the hostile environment and to provide the surface roughness needed for the mechanical bonding of the zirconia top coat subsequently sprayed onto it.

Early studies[8][9][10] on TBCs have proven that oxidation of the bond coat is the dominant degradation mechanism of TBCs and operationally induced stresses can only exert a complementary effect to the TBCs' failure. This implies that the performance of TBCs might be improved if the oxidation rate of the MCrAlY bond coat were decreased, thereby decreasing the bond coat oxidation stresses which can induce spalling of the zirconia top coat. Based on this point of view, some “sealing concepts” on the zirconia top coat or MCrAlY bond coat were proposed and investigated. Zplatynsky[8] proposed that the formation of a glazed layer on the surface of the zirconia top coat by a laser-glazing treatment could significantly reduce salt penetration through the top coat in a burner rig flame with 100 ppm Na fuel equivalent and hence result in an increase of TBC life. Eaton and Novak[10] reported the idea of substituting an alumina/CoCrAlY composite for the zirconia/CoCrAlY composite as an intermediate graded layer of gas-path sealing coating. The Al₂O₃ particles act as a barrier to oxygen reaching the CoCrAlY within the bond coat. Also, Mantyla et al.[11] proposed that the open porosity of plasma sprayed coatings can be effectively sealed by a dense chemical vapor deposited Al₂O₃ layer on their surfaces.

In this study, a new sealing concept for TBCs was attempted, i.e., an intermediate Al₂O₃ oxygen-diffusion barrier was coated onto the surface of Ni-22Cr-10Al-1Y bond coat by chemical vapor deposition (CVD) before subsequent overlaying of the zirconia top coat. As a result, oxidation of the bond coat might be depressed by the chemical vapor deposited Al₂O₃ layer due to the comparatively lower diffusivity of oxygen in Al₂O₃[12]. The oxygen-diffusion-barrier process for TBCs attempted in this study is characterized as follows:

1. The diffusion-barrier layer was applied between the zirconia top coat and the bond coat. As a result, the most severe part of the thermal shock stress was sustained and accommodated by the zirconia top coat. This stress is attenuated when transferred to the CVD Al₂O₃ layer due to the lower heat transfer rate of the zirconia thermal barrier.
2. The surface of the bond coat could be perfectly sealed by the CVD Al₂O₃ layer, which is thin (about 3~7 µm), dense and continuous.
3. Free expansion/contraction of the zirconia top coat was not hindered and stresses encountered during heating or cooling of TBCs can be relieved as in the case of traditional duplex zirconia/MCrAlY TBCs.

In this study, the effects of the CVD process para-
imeters, namely, deposition temperature, deposition time, CVD deposition pressure and total gas flow rate, on the performance of proposed triplex ZrO₂–8 mass% Y₂O₃/CVD Al₂O₃/Ni–22Cr–10Al–1Y thermal barrier coatings were evaluated by thermal cycling tests at 1273 K. The growth rate of CVD Al₂O₃, the effectiveness of CVD Al₂O₃ layer as an oxygen-diffusion-barrier on the surface of the bond coat and the optimal combinations of the CVD process parameters on the performance of TBCs were determined in this study.

II. Experimental Procedure

1. Specimen preparation

Investment cast Mar-M247 superalloy (Table 1) was used as substrate material and cast into airfoil specimens. As cast specimens were grit blasted and placed into a vacuum plasma spraying system (VPS) for the overlaying of Ni–22Cr–10Al–1Y bond coat (~0.15 mm). The VPS parameters applied in this study for the overlaying of bond coat are listed in Table 2. Part of the specimens were further coated with Al₂O₃ in a hot-wall chemical vapor deposition (CVD) system. The apparatus for CVD process and the deposition parameters will be briefly described in the next paragraph. All the specimens, whether or not deposited with Al₂O₃, were then sprayed with 8 mass% yttria partially stabilized zirconia (8 mass% Y-PSZ) top coat (~0.25 mm) in an atmospheric plasma spraying system with the deposition parameters listed in Table 3. After spraying with the top coat, the TBC specimens were subjected to heat treatment at 1393 K in argon for 7.2 ks to promote diffusion bonding between the bond coat and substrate.

2. Deposition of Al₂O₃ layer by CVD

The apparatus for CVD process used in this study is shown in Fig. 1. The specimens sprayed with Ni–22Cr–10Al–1Y bond coat were inserted in the reactor and heated in hydrogen atmosphere to the deposition temperature. After reaching the deposition temperature, a gas mixture of AlCl₃/H₂, CO₂, and H₂ were introduced into the reactor to deposit Al₂O₃ on the bond coat surface. The AlCl₃ gas was produced from the sublimation of anhydrous AlCl₃ heated to 403 K with H₂ as a carrier gas.

For the deposition of CVD Al₂O₃, we used the total gas flow rate: 16.7 × 10⁻⁶, 25 × 10⁻⁶, 33.4 × 10⁻⁶ and 41.7 × 10⁻⁶ m³ s⁻¹, the molar fraction of AlCl₃: 5.62 × 10⁻³, and H₂/CO₂: 5. The total pressure in the reactor was maintained at about 14.7, 34.7, 54.7, and 74.7 kPa by adjusting a needle valve and operating a vacuum pump. The specimens were coated at the deposition temperatures (i.e. 1073, 1123, 1173, 1223, and 1273 K), for a specified deposition time (from 1.8 to 5.4 ks), and then cooled to room temperature in the hydrogen atmosphere.

3. Tests

The heat treated specimens were subjected to a thermal cyclic test at 1273 K in an atmospheric heating furnace (1 cycle=0.6 ks heat-up to temperature, 3.6 ks holding at temperature, and 0.6 ks forced air cooling to room temperature). The coating was considered to have failed when a visible crack or delamination of the top coat was observable by the naked eye after the specimen was cooled to room temperature. The number of cycles elapsed at failure for each specimen was recorded as TBC lifetime or cyclic life. Weight of the TBC specimen was recorded by a digital balance, with an accuracy to ±0.5 mg, cycle by cycle after the specimen was cooled to ambient temperature.

III. Results and Discussion

1. Microstructures of ZrO₂–8 mass% Y₂O₃/CVD Al₂O₃/Ni–22Cr–10Al–1Y thermal barrier coatings

A cross-sectional view of ZrO₂–8 mass% Y₂O₃/CVD Al₂O₃/Ni–22Cr–10Al–1Y thermal barrier coatings is shown in Fig. 2. The thickness of Al₂O₃ deposited in this study was calculated from mass gain; dependent on the various combinations of applied CVD parameters, the thickness was typically about 2–10 μm. As shown in Fig. 2, the results of EPMA analyses show that the dark interlayer between top coat and bond coat is a dense, thin and continuous Al₂O₃ layer which was deposited on the surface of the bond coat as an oxygen-diffusion-barrier.
to protect the bond coat from oxidation. It is noticeable in Fig. 2 that the CVD Al₂O₃ layer made intimate contact with the zirconia top coat, and the surface roughness of the as-sprayed Ni–22Cr–10Al–1Y bond coat was maintained after the deposition of Al₂O₃. It is thus presumed that the application of CVD Al₂O₃ on the surface of the bond coat before overlaying with the top coat should not be detrimental to the bonding between the top coat and bond coat.

2. Effectiveness of CVD Al₂O₃ layer as an oxygen diffusion barrier

The results of thermal cyclic tests at 1273 K for TBC specimens showed that CVD Al₂O₃ coatings on the surface of the bond coat significantly reduced the oxidation rate of the bond coat when compared with uncoated specimens. After oxidation at 1273 K for 1 cycle, the mass gain of the CVD Al₂O₃ coated specimens was remarkably lower than that of the uncoated specimens as shown in Fig. 3. Also, for the CVD Al₂O₃ coated specimens, the mass gain of the first cycle decreased as the thickness of CVD Al₂O₃ was increased; i.e., the thicker CVD Al₂O₃ layers exhibited better impermeability to the penetration of oxygen to oxidize the bond coat.
As summarized by Kofstad\textsuperscript{(19)}, the growth of Al\textsubscript{2}O\textsubscript{3} grains in protective coating of Al\textsubscript{2}O\textsubscript{3} on aluminum alloys formed by oxidation occurred mainly by gaseous or ionic penetration of oxygen through the grain boundaries. The transport of oxygen, resulting in oxidation of the bond coat and mass gain of CVD Al\textsubscript{2}O\textsubscript{3} coated specimens, measured from cyclic oxidation tests as shown in Fig. 3, is assumed to occur via a similar route.

3. Results of thermal cyclic tests

Effects of the four CVD process parameters, i.e., deposition temperature, deposition time, deposition pressure and total gas flow rate of CVD species, on the cyclic life of ZrO\textsubscript{2}-8 mass\% Y\textsubscript{2}O\textsubscript{3}/CVD Al\textsubscript{2}O\textsubscript{3}/Ni-22Cr-10Al-1Y thermal barrier coatings were evaluated by thermal cyclic tests at 1273 K in this study.

(1) Effects of deposition temperature

The growth rate of Al\textsubscript{2}O\textsubscript{3} increased linearly with increasing deposition temperature, as shown in Fig. 4. The relationship between cyclic life and deposition temperature of CVD Al\textsubscript{2}O\textsubscript{3} is shown in Fig. 5. Under the growth condition of 14.7 kPa deposition pressure and 25.0 x 10\textsuperscript{-6} m\textsuperscript{3}\textpercm\textsuperscript{2} s\textsuperscript{-1} total gas flow rate for 3.6 ks, the cyclic life of TBC specimens whose Al\textsubscript{2}O\textsubscript{3} was deposited at 1273 K was remarkably higher than the uncoated specimens. However, for the specimens whose Al\textsubscript{2}O\textsubscript{3} was deposited at 1073, 1123, 1173 and 1223 K, about the same number of cycles as the TBC specimens without Al\textsubscript{2}O\textsubscript{3} was endured. The SEM morphology of the corresponding α-CVD Al\textsubscript{2}O\textsubscript{3} (determined by X-ray diffraction) grown at various temperatures is shown in Fig. 6. This figure shows that the morphology of CVD Al\textsubscript{2}O\textsubscript{3} varies in a regular progression from uniformly faceted shape to discontinuous dome shaped grains as the deposition temperature decreases. The cause of this transition has been explained elsewhere\textsuperscript{(20)}. Apparently, the effect of deposition temperature on the TBCs' cyclic life is associated with the morphology of CVD Al\textsubscript{2}O\textsubscript{3} and the residual stress owing to deposition, which could influence the stress state of the triplex ZrO\textsubscript{2}-8 mass\% Y\textsubscript{2}O\textsubscript{3}/CVD Al\textsubscript{2}O\textsubscript{3}/Ni-22Cr-10Al-1Y system considered. The stress state of the current TBCs may be further complicated by creep of the bond coat\textsuperscript{(19)}, growth of oxide scales\textsuperscript{(19)(18)}, and thermal mismatches among the top coat, intermediate CVD Al\textsubscript{2}O\textsubscript{3} and bond coat\textsuperscript{(7)(13)}, thus a further study is needed.

(2) Effects of deposition time

The effects of deposition time of CVD Al\textsubscript{2}O\textsubscript{3} on cyclic life of TBCs is shown in Fig. 7. As shown in Fig. 8, increasing the deposition time resulted mainly in an increase in the thickness of CVD Al\textsubscript{2}O\textsubscript{3}. The failure of the specimen whose Al\textsubscript{2}O\textsubscript{3} was deposited for 1.8 ks (Al\textsubscript{2}O\textsubscript{3} layer thickness = 2.61 μm) was presumed to be due to the very thin Al\textsubscript{2}O\textsubscript{3} layer formation on the bond coat owing to the limited formation time. It would be believed that CVD Al\textsubscript{2}O\textsubscript{3} layer is incapable of protecting bond coat from oxidation. As shown in Fig. 7, the life of specimens whose Al\textsubscript{2}O\textsubscript{3} was deposited for 2.7, 3.6 and 4.5 ks (corresponding to scale thicknesses of 2.86, 4.94 and 5.88 μm, respectively) endured remarkably more cycles than specimens not coated with Al\textsubscript{2}O\textsubscript{3}. However, as the thickness of Al\textsubscript{2}O\textsubscript{3} was further increased, the CTE mismatch stresses encountered during the cyclic tests was also increased\textsuperscript{(17)(18)}, i.e., the beneficial decrease in oxidation rate of pre-CVD Al\textsubscript{2}O\textsubscript{3} treated bond coat may be compromised by the undesirable increase in buckling stresses during the cooling cycle induced by a thicker CVD Al\textsubscript{2}O\textsubscript{3} layer. As a result, the specimen whose Al\textsubscript{2}O\textsubscript{3} was deposited for 5.4 ks (Al\textsubscript{2}O\textsubscript{3} layer thickness = 7.78 μm) exhibited no improvement in cyclic life as shown in Fig. 7.

(3) Effects of deposition pressure

As shown in Fig. 9, the TBC specimens whose Al\textsubscript{2}O\textsubscript{3} was deposited at 1273 K endured more cycles than those deposited at 1073 K within the deposition pressure range tested in this study. Figure 9 further shows that for Al\textsubscript{2}O\textsubscript{3} deposited at 1273 K, the improvement was more obvious when the deposition was taken place at 14.7 and 74.7 kPa than at intermediate pressures. Since the as-deposited weight gain was larger for specimens deposited at 34.7 and 54.7 kPa (Fig. 10), the CTE mismatch stresses for the specimens should be larger than those specimens whose Al\textsubscript{2}O\textsubscript{3} was deposited at 14.7 and 74.7 kPa, i.e., with thinner Al\textsubscript{2}O\textsubscript{3} layers.

In addition to the consideration of deposited Al\textsubscript{2}O\textsubscript{3}
thickness, the role of morphology may again be equally important. Figure 11 compares the morphology of deposited CVD Al₂O₃ at the deposition pressures of 14.7 and 54.7 kPa. As shown in this figure, the morphology of the latter appears discontinuous, non-uniform and overly thick. The previous research indicated that as the deposition pressure was increased, the input gaseous species flowed in a free convection state which was detrimental to thickness uniformity of CVD Al₂O₃ layers⁹. The undesirable non-uniform thickness of Al₂O₃ resulting from higher deposition pressures is believed to induce stress concentrations in the Al₂O₃ layer which
16.7 × 10^{-6} \text{ m}^3 \text{s}^{-1} to 33.4 × 10^{-6} \text{ m}^3 \text{s}^{-1}. Further increase in gas flow rate beyond 33.4 × 10^{-6} \text{ m}^3 \text{s}^{-1} recorded no proportional increase in growth rate. It is rationalized that surface-reaction controlled growth has been substituted for mass transfer diffusion controlled growth as the limiting growth rate mechanism of the CVD layer at a high total gas flow rate. All of the specimens were deposited with Al_2O_3 for 3.6 ks, therefore, according to Fig. 12, the thickness of CVD Al_2O_3 increased with the total gas flow rate until the surface-reaction controlled growth was the dominant growth mechanism for depositing CVD Al_2O_3. The thickness of the CVD Al_2O_3 layer deposited at the 16.7 × 10^{-6}, 25.0 × 10^{-6}, 33.4 × 10^{-6} and 41.7 × 10^{-6} \text{ m}^3 \text{s}^{-1} total gas flow rates are 2.94, 4.94, 7.16 and 7.12 \mu \text{m}, respectively. The SEM morphology of CVD Al_2O_3 deposited at the total gas flow rate of 16.7 × 10^{-6} and 33.4 × 10^{-6} \text{ m}^3 \text{s}^{-1} is shown in Fig. 13(a) and (b), respectively. At a total gas flow rate of 16.7 × 10^{-6} \text{ m}^3 \text{s}^{-1}, the deposited CVD Al_2O_3 grains were coarser. At 33.4 × 10^{-6} \text{ m}^3 \text{s}^{-1} more CVD Al_2O_3 grains per unit area with the finer grain can be observed. The effect of total gas flow rate on the CVD Al_2O_3 grain density appears to be a problem of nucleation and growth. Increasing the total gas flow rate increases either the nucleation rate or the advantageous ratio of nucleation becomes detrimental to the specimen life.

For the specimens whose Al_2O_3 was deposited at 1073 K, since about the same weight gain of Al_2O_3 resulted for all four deposition pressures (Fig. 10), the life of specimens coated with different deposition pressures endured about the same number of cycles (Fig. 9).

(4) Effect of total gas flow rate

As shown in Fig. 12, the growth rate of CVD Al_2O_3 increased as the total gas flow rate was increased from

![Fig. 11 Comparison of the SEM morphology of CVD Al_2O_3 deposited at: (a) 14.7 kPa and (b) 54.7 kPa, other conditions being 1273 K and 25.0 × 10^{-6} \text{ m}^3 \text{s}^{-1} total gas flow rate.](image)

![Fig. 13 Comparison of the SEM morphology of CVD Al_2O_3 deposited at total flow rates of: (a) 16.7 × 10^{-6} \text{ m}^3 \text{s}^{-1} and (b) 33.4 × 10^{-6} \text{ m}^3 \text{s}^{-1} (deposition pressure=14.7 kPa, deposition temperature=1273 K, deposition time=3.6 ks).](image)

Fig. 12 The growth rate of CVD Al_2O_3 as a function of total gas flow rate of CVD species.
rate to growth rate. The relationship between the cyclic life of TBCs and the total gas flow rate of CVD Al₂O₃ is shown in Fig. 14. Except for the specimens deposited with a total gas flow rate of $16.7 \times 10^{-6}$ m$^3$ s$^{-1}$, the specimens coated with CVD Al₂O₃ endured remarkably more cycles than uncoated specimens. As mentioned in section 3-(2), a too thin Al₂O₃ layer is incapable of protecting bond coat from oxidation. Since a variation of the total gas flow rate apparently has not significantly changed the morphology of the CVD Al₂O₃, the specimen whose Al₂O₃ was deposited at the total gas flow rate of $16.7 \times 10^{-6}$ m$^3$ s$^{-1}$ failed to improve the performance of TBCs might be attributed to its thin thickness (2.94 μm). Bryant and Kropfi found that the thickness of coating tend to exhibits non-uniformity at low gas flow velocity and mass transfer rate$^{19}$. Thus the cyclic life of the TBC specimens with intermediate CVD Al₂O₃ was found to increase with increasing total gas flow rate as indicated in Fig. 14.

4. Optimization on the thickness of CVD Al₂O₃

The thickness of CVD Al₂O₃ is important in the suppression of oxidation of the bond coat, as discussed previously; however, the accompanying CTE (coefficient of thermal expansion) mismatch stresses, which are a function of scale thickness$^{17,18}$, must also be considered, and require a compromise in the thickness of the CVD Al₂O₃.

The life of the present CVD Al₂O₃ modified TBCs depends not only on the thickness but also on the morphology of the CVD Al₂O₃. In Fig. 15, the life of TBCs is plotted against the thickness of CVD Al₂O₃ but including only the data on CVD Al₂O₃ deposited at 1273 K and 14.7 kPa, on the assumption that the variation of TBC life plotted in this manner is a function of the thickness of CVD Al₂O₃ for samples with similar morphologies. For the specimens whose CVD Al₂O₃ thickness falls within the range from about 3 to 7 μm as indicated in Fig. 15, the TBC specimens survived about 5 times as many cycles as those without CVD Al₂O₃. A too thin CVD Al₂O₃ layer is incapable to hinder oxygen transport through the CVD Al₂O₃ layer to oxidize the bond coat. In addition, the CTE mismatch stress caused by CVD Al₂O₃ layer is unavoidable. Therefore, the combined growth stress due to severe bond coat oxidation and CTE mismatch stress led to the failure of TBC specimens with the Al₂O₃ layer less than 3 μm thick. However, the reason why the specimens whose CVD Al₂O₃ thickness exceeded about 7 μm failed to improve the lifetime of TBC specimens is due to the overly thick Al₂O₃ in these specimens which generated an excessively high CTE mismatch stress to cause the failure of the system.

IV. Summary

The effects of the CVD process parameters, i.e., deposition temperature, deposition time, deposition pressure and total gas flow rate of CVD species, on the performance of triplex ZrO₂-8 mass% Y₂O₃/CVD Al₂O₃/Ni-22Cr-10Al-1Y thermal barrier coatings at 1273 K were evaluated in this study. The application of CVD Al₂O₃ layer can effectively decrease the oxidation rate of Ni-22Cr-10Al-1Y bond coat, resulting in a remarkable increase in the cyclic life of TBCs when compared with specimens not coated with CVD Al₂O₃. However, if not properly controlled, the application of Al₂O₃ might also induce undesirable effects to TBCs, e.g., undesirable Al₂O₃ microstructures and hence an increase in operationally induced stresses, which might result in either a decrease in the capability of Al₂O₃ to protect the bond coat from oxidation or even a premature failure of TBCs during operations.

Based on the thermal cyclic tests conducted at 1273 K in this study, the most optimal combination of CVD Al₂O₃ parameters to the cyclic life of triplex ZrO₂-8 mass% Y₂O₃/CVD Al₂O₃/Ni-22Cr-10Al-1Y thermal barrier coatings is concluded as follows: deposition temperature=1273 K, deposition time=3.6~4.5 ks, deposition pressure=14.7 kPa, and total gas flow rate >25.0 × 10^{-6} m³ s⁻¹. For TBC specimens whose Al₂O₃ was deposited at 1273 K and 14.7 kPa, there existed an optimum thickness of CVD Al₂O₃ layer within the range from about 3 to 7 μm which remarkably improved the performance of TBCs.

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