Life Time of Triplex System Thermal Barrier Coatings with NiCoCrAlY Bond Coat Exposed to Cyclic Oxidation

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ABSTRACT

Thermal Barrier Coatings (TBCs) is one of the surface modification techniques. Thermal barrier coat in triplex structures were deposited on hastalloy x, Inconel 617 and IN 738. The ceramic coat was partially stabilized zirconia (YSZ 7-8% Y$_2$O$_3$) and bond coat of nickel base alloy, namely NiCoCrAlY alloy. The triplex structure was designed to investigate the interdiffusion of elements through the bond coat alloy under and over the ceramic coat which is believed to be one of failure mechanisms of TBCs during cyclic oxidation. Optical microscopy, Scanning Electron Microscopy (SEM) and X-Ray Energy Dispersive analysis (EDX) were used in this investigation.

Key Words: plasma spraying, Thermal Barrier Coating, Triplex system, Cyclic oxidation, Interdiffusion, EDX analysis

INTRODUCTION

Evaluation of the performance of MCrAlY bond coat to protect engineering components coated with thermal barrier coatings (TBC’s) when exposed to cyclic oxidation in air and in presence of aggressive species such as S and Na is of great importance. Thermal barrier coatings in triplex structures were deposited on Inconel 617 and IN 738. The ceramic coating for all specimens was partially stabilized zirconia (YSZ) with 7-8% Y$_2$O$_3$; the bond coating was NiCoCrAlY alloy. The effect of TBC’s structure and cyclic oxidation mode on the failure characteristic of the bond coating were discussed. Optical microscopy, Scanning Electron Microscopy (SEM) were used in the investigation. TBCs often faces the problems of spallation and cracking in service, due to the mismatch of thermal expansion coefficient between YSZ and the nickel base alloy bond coat. This problem can be eliminated by using graded TBC’s.$^{(1-10)}$

It is known that the dominant failure mechanism on cooling in the temperature range from 930 °C to 1100°C is by spallation of the ceramic coating due to cracking either within the ceramic top layer or the thermally grown oxide (TGO)$^{(11-15)}$. In this study a TBC system designated as triplex TBC was designed to get more information about the effect of TGO on the delamination.
EXPERIMENTAL WORK

The plasma sprayed zirconia was partially stabilized with 7% wt $Y_2O_3$- agglomerated and sintered with particle size $\sim 45+10\mu m$. The nominal composition of the bond coating was Ni- 22Co- 17Cr-12.5Al- 0.43Y.

TBC’s triplex system as deposited as shown in Fig.1 were tested to investigate the oxidation characteristics of the bond coating alloy in both below and over the ceramic coating and the stresses generated in this bond coating.

The TBC’s were deposited over three Ni-base alloys, namely Hastelloy x, Inconel 617 and IN 738 with vacuum plasma spraying machine (VPS), from plasma – technique AG, Switzerland. The spraying parameters were power 55 KW and current was 720 A, carrier gas was Ar with 1.7 SLPM and plasma gas was 20 SLPM Ar, 8 SLPM $H_2$, 25 SLPM He. Plasma spraying was conducted at 100mbar pressure, and the gun to workpiece distance was 250 mm.

![Fig.1: Optical graph of triplex system as deposited](image)

**Oxidation experiments**

In the oxidation experiments, specimens were heated at 1100°C for one hour then cooled to room temperature and recycled with the same routine until the beginning of spallation.

In this work we study the effect of substrate oxidation on the coating life of TBC triplex system. The samples were investigated for the oxidation resistance of the substrate hestalloy x, IN 738 and Inconel 617 with TBC’s over nickel base alloys namely NiCoCrAlY.

The specimens were plasma sprayed in the Institute of materials of energy systems, IWE- 1/FZJ, Juelich, Germany.

**RESULTS AND DISCUSSION**

The service life of plasma sprayed Triplex system thermal barrier coating TBC is closely related to thermal cycling resistance, oxidation resistance of bond coat and the thermal expansion mismatch strains.
Oxidation conditions:

The failure mechanism in triplex TBC’s can be due to the propagation of the spallation of YSZ. Also it can be due to the propagation of internal cracks through the coating. At a critical value of internal cracks through the coating and at a critical value of crack length, unstable crack propagation occurs. The effect of substrate composition and inter-diffusion of elements in bond coating and formation of TGO and the life of coating is explained based on the results of previous researches \(^{16-18}\).

Effect of substrate in triplex system

In this study, three different substrates were tested with the same bond coat NiCoCrAlY to investigate the effect of substrate on life time of TBC’s as shown in Table 1.

Table 1: Number of cycles to failure triplex system

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Bond coat</th>
<th>No. cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>IN 617</td>
<td>NiCoCrAlY</td>
<td>85</td>
</tr>
<tr>
<td>IN 738</td>
<td>NiCoCrAlY</td>
<td>45</td>
</tr>
<tr>
<td>Hastelloy x</td>
<td>NiCoCrAlY</td>
<td>210</td>
</tr>
</tbody>
</table>

From Table 1: It is firstly noticed that the substrate hastelloy x has the highest number of cycles to failure than Inconel 617, In 738. This may be due to the minimum diffusion between substrate and bond coat. The percentage of element Ni is approximately the same in substrate and bond coat NiCoCrAlY as shown in EDX analysis Fig. 2. The differences in chemical activities of elements in the bond coat and substrate lead to interdiffusion. Ni in the superalloy substrate diffuses towards the bond coat, and Cr, Al in the bond coat diffuses towards the substrate.

Different substrates mean different physical properties such as thermal expansion coefficient and thermal conductivity, and different micro-hardness. Also different chemical composition means different mutual effect between substrate and bond coat. The results show different number of cycles to failure of different substrates with the same bond coat, due to the difference in physical properties.
Cross sections were examined by SEM and EDX analysis. The results of as sprayed before and after thermal cycling at 1100°C of the TBC triplex system with Zr$_2$O$_2$-Y$_2$O$_3$ ceramic coat and NiCoCrAlY bond coat are shown in Figure (3, 4). From Fig. 2 it can be seen that elements Ni, Co, Cr and Al are uniformly distributed throughout the bond coat, in the as sprayed samples. After thermal cycling of the TBC, the development of several microstructural features, which may be related to the failure of TBC, were examined.
Growing of TGO and depletion of β phase in the bond coat induced micro cracking at the YSZ/TGO interface. The composition of TGO from EDX analysis is shown in Fig. 4. Bond coat interface, and Ni/Co rich TGO is formed due to internal oxidation of bond coat. Growing TGO increases the strain energy available for the crack propagation during the spallation. Damage at the YSZ/TGO interface during thermal cycling can be explained as that during high temperature thermal cycling. Thermally activated processes possibly produced various stresses, such as bond coat oxide growth stress and phase transformation in YSZ induced stress caused by volume difference between tetragonal and monoclinic phases, and they are concentrated near the top coat – bond coat interface which cause spallation of TBC from the substrate (18).

EDX analysis after thermal cycling of a triplex system with NiCoCrAlY bond coat and IN 738 substrate is shown in Fig.4. Ni and Cr diffuse from bond coat toward the ceramic coat and Al diffuses in bond coat to the upper end and form TGO which is composed mainly of Al₂O₃ as the EDX analysis at point 4 shows. It can be seen that the content of Al is 49 wt. % while the content of Al in the as sprayed is 10.6 wt.%. this is attributed to the fast diffusion of Al which leads to the formation of brittle phase may that cause decrease in life of time of TBC.

The rapid oxidation of bond coat NiCoCrAlY is inhibited by the formation of a layer of Al₂O₃. Al₂O₃ may prevent the coating from further oxidation. At high temperature, the oxides of Al₂O₃ or Cr₂O₃, will cover the bond coat NiCoCrAlY, phases of Ni and Co may be formed and lot of island-like phases are shown in the matrix (19).
The difference in coefficient of thermal expansion value between YSZ ceramic coat and NiCoCrAlY bond coat is an important factor in failure coating mechanism. The difference increases significantly with an increase in temperature and results the cracks and spallation, as shown in SEM and optical graph Fig (5, 8). There for in the triplex system composed of NiCoCrAlY and YSZ, a large thermal mismatch will be generated between two layers of bond coat with variation of temperature. This large thermal mismatch will cause a large thermal residual stress, which will result in the formation of cracks or spallation of the coating (20).

Fig. 5: SEM of bond coat NiCoCrAlY deposited on IN 738 triplex system after thermal cycling oxidation

After oxidation at temperature 1100°C TGO formed between bond coat and ceramic coat, a -Al₂O₃ was a major phase. It is generally accepted that the presence of some other phases as NiAl₂O₄ on the outer surface of oxide scale means that Al-depletion occurred and Ni diffused to surface and reacted with oxygen at scale interface. And then NiO reacted with the existing a -Al₂O₃ to produce NiAl₂O₄ at this temperature, this means the transition of oxidation mechanism from unstable phase to stable phase. This change of major oxide phase indicates that Al-depletion rate was rapid due to fast oxidation rate of Al (21). It is obvious from SEM and EDX analysis of elements at points 1, 2, 3 Figure (6) and EDX analysis Fig. 7.

Fig 6: SEM of top bond coat NiCoCrAlY deposited on IN 738 triplex system after thermal cycling oxidation at 1100°C
Fig. 7: EDX of top bond coat NiCoCrAlY deposited on IN 738 triplex system after thermal cycling oxidation at 1100°C.

Results show that the bond coat NiCoCrAlY deposit on IN738 exhibits a less number of cycles to failure than NiCoCrAlY deposited on substrate Inconel 617. This is clear from comparing EDX analysis and SEM of triplex system after thermal cycling Fig. 9 and 10 with nominal composition. It can be observed that at point 4 the Al content is 41.16 wt% in the oxide layer formed at bond coat ceramic coat interface, which is much higher than initial value of as sprayed and nominal composition of Al 12.3wt%.

On the other hand the value of Ni is 13.78 wt% at point 4 and at point 3 it is 48.83 wt%, in point 1 it is 50 wt% the value as sprayed and nominal composition of Ni in alloy was 46.76 wt%. All the data indicated that the Ni element begins to diffuse from the area near substrate to area near ceramic coat during oxidation process.

Interdiffusion from bond coat to substrate is clear at point 1 where Co content changed to less than its nominal composition. Al depleted zone is clear from figure 10 near substrate, after the depletion of Al-rich ß phases in the bond coat \(^{(22)}\).
Fig. 9: EDX analysis of bond coat NiCoCrAlY deposited on Inconel 617 in triplex system after thermal cycling oxidation at 1100°C

The darker areas indicate regions of lower atomic mass (i.e. oxides), while the bright regions indicate regions higher atomic mass i.e. the zirconia. Voids and cracks in ceramic coat may be formed due to oxidation (internal and external) and phase transformation $\text{ZrO}_2-\text{Y}_2\text{O}_3$ (23).

Fig. 10: SEM of bond coat NiCoCrAlY deposited on substrate Inconel 617 in triplex system after thermal cycling oxidation at 1100°C

Figure 11 shows the ceramic coat after heat exposure extensive oxidation. The darker areas indicate regions of lower atomic mass (i.e. oxides), while the bright regions indicate regions higher atomic mass i.e. the zirconia. Voids and cracks in ceramic coat may be formed due to oxidation (internal and external) and phase transformation $\text{ZrO}_2-\text{Y}_2\text{O}_3$ (23).
Fig. 11: SEM of ceramic coat $\text{ZrO}_2$-$\text{Y}_2\text{O}_3$ near bond coat of NiCoCrAlY deposited on substrate Inconel 617 in triplex system after thermal cycling oxidation

From Figures 12, 13 EDX analysis and SEM of top bond coat near ceramic coat show that at point 4 the Al content is 5.08 wt%, at point 3 the content is 9.42 and at point 2 is 7.98 wt%. The consequent reduction of aluminum at the oxide – coating interface triggered intrinsic chemical failure, manifested by the formation of a layer of Cr,Al,Ni-rich oxides\(^{(23)}\).

Associated with this process of chemical failure, was the formation the outer porous layer of Ni,Cr, Co, rich oxides forming hard phases which may be causes of cracks\(^{(24)}\). Also the performance of plasma sprayed coating during thermal cycling is related directly to the generation of thermal fatigue cracks caused by high residual stress in coatings. The triplex coating was more prone to surface cracking. The surface radial/tangential stresses and the axial/shear stresses at the edge of the specimen were always tensile during the cooling process. Exposures of the ceramic layer of YSZ in triplex system to thermal cycling causes spallation due to differences in thermal expansion coefficients of different layers of the coating\(^{(25)}\).

Fig. 12: EDX analysis of top bond coat NiCoCrAlY and top near ceramic coat deposited on substrate Inconel 617 after thermal cycling oxidation triplex system
CONCLUSION

Thermal barrier coatings lifetimes are dependent on many factors, which are greatly affected by the chemistry of bond coat and substrate. Thermal cycling transfers the bond coat material from metastable phase to stable phase and hard phases may be formed which influence the lifetime of TBC’s. At high temperature the lifetime of TBC’s is affected by phase transformation of $\text{ZrO}_2$, and thermally growing oxide TGO between bond coat and ceramic coat. Interdiffusion through bond coat and at bond coat/substrate interface is one of the main causes of TBC’s failure. The results show that the best substrate of triplex system in oxidation experiment is hastelloy x with NiCoCrAlY bond coat.

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