

High Temperature Oxidation Study of Plasma Sprayed Zirconia (Yttria Stabilized) Ceramic Thermal Barrier Coating

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ABSTRACT: Thermal barrier coating (TBC) system protects the turbine blade against high temperature corrosion. It consists of a MCrAlY bond coat, a ceramic top layer (8-YSZ) and super alloy substrate. The oxidation resistance of the TBC system is based on the MCrAlY coating which has a tendency of formation of the α -Al₂O₃ in the steady state of oxidation. This α -Al₂O₃ layer protects the turbine blade against oxidation as well as it is the main cause of the strain incompatibility that can drive coating spallation. The α -Al₂O₃ grows very slowly between the metallic bond coating and the ceramic top coating and is thermodynamically stable. In the present work high temperature thermo gravimetric oxidation study at 900°C to 1200°C was carried out on the 3 different types of the sample like superalloy substrate (Inconel-600), superalloy substrate coated with MCrAlY and/or 8-YSZ.

The results shows that 8-YSZ coating has very low oxidation rate as compared to bond coated as well as uncoated samples, and from these result parabolic rate constant k_p and activation energy is also calculated

KEYWORDS: 8-YSZ, TBC, MCrAlY, α -Al₂O₃, XRD.

I. INTRODUCTION

Plasma sprayed thermal barrier coating are traditionally applied to gas turbine engine blades and vanes in order to reduce their operating temperature and increase the component durability.^[1] A typical duplex system consists of thermally insulating ZrO₂ alloy top coat applied over an oxidation resistance MCrAlY (M= Ni and /or Co) bond coat.^[2,4]

The thermal properties of the TBC need to be investigated extensively because these coating are used extensively at high temperature and severe thermal loads .the service life of plasma sprayed TBC is closely related to thermal cycling resistance, oxidation resistance of the bond coat and the thermal expansion mismatch strains, etc.^[4,5]

II. EXPERIMENTAL WORK

The substrate were 1 cm X 1cm X 1.5 mm samples of superalloy, Inconel-600 (C-0.13%, Si-0.17%, Mn-0.66%, S-0.0085%,Cr-16.97, Mo-0.038%, Co-0.047%, Al-0.010%, Fe-8% and Ni- Bal, wt %) which were degreased and grit blasted by alumina grit of size 24 mesh before spraying. The powder materials for spraying were an 8-wt % Y₂O₃ stabilized ZrO₂ as a ceramic coat and inert gas atomized MCrAlY powder (Amdry 962, SM AG, Switzerland) as a bond coat used as a feedstock for coating preparation. Plasma spraying is carried out by using Sulzer Metco (SM 204 NS). The plasma spraying parameter is as follows:

Parameters	Bond coat (AMDRY 962)	Thermal Barrier Coat (8-YSZ)
Primary gases	N ₂ (3.45 bar) 100 m ³ /h	Ar (6.9 bar) 80 m ³ /h
Secondary gases	H ₂ (3.45 bar), 15 m ³ /h	H ₂ (3.4 bar), 15 m ³ /h
Carrier gas flow rate (m ³ /h)	37	37
Arc current (amps)	500 - 550	600
Arc voltage(volts)	74-80	64- 70
Particle velocity (m/s)	250	250-600
Spray distance mm	125	64
Porosity (volume %)	1-2	2-5
Coating thickness (μ)	100-125	200-250

After preparing three different types of the sample like uncoated, bond coated, and bond coat with YSZ coated Isothermal oxidation tests were carried out on these samples at 900, 1000, 1100 and 1200°C, with oxidation there is gain in weight of the sample that could be monitored from measuring the elongation of silica spring sensitivity of the balance used was 0.02139 mg and the gas flow rate is 180-200 bubbles/ min. At the end of the experiment, the test samples are removed from the furnace and placed into cooler zone, and these test samples are stored carefully in the desiccators. The oxidation behaviour was evaluated by the mass gain of the samples

After the tests, the phase compositions of deposited coatings were identified by X-ray diffraction (Make: - Pan Analytical, Japan). The morphologies of TBCs and the chemical compositions of the thermally grown oxides (TGO), in cross-section, were determined using an Analytical scanning electron microscope (model JEOL- 6360 A), equipped with an X-ray energy-dispersive analyzer (EDS).

A. UNCOATED BASE METAL (INCONEL-600)

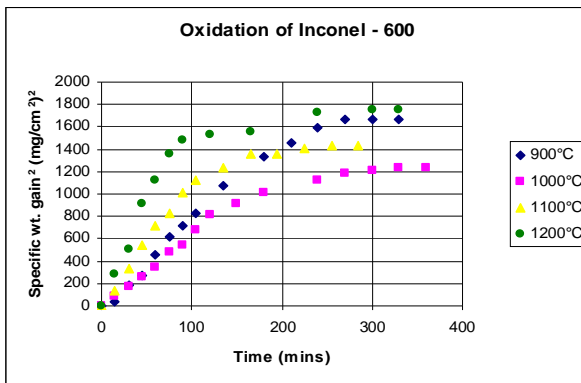


Fig.1: Plot of Square of Specific wt gain Vs Time at different temp.

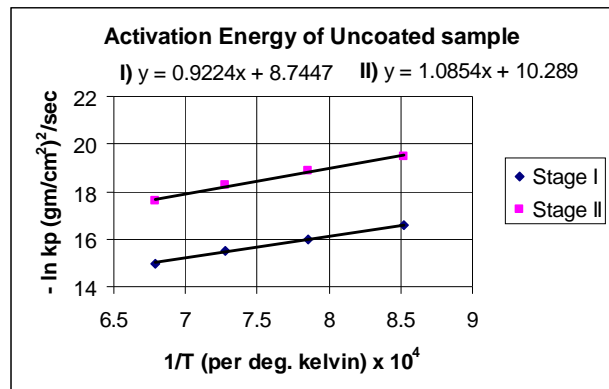


Fig.2: Plot of ln kp Vs 1/T for uncoated sample

It will be seen from the Fig.1 that, there is a linear relationship between squares of wt gain against time, confirming the parabolic law of oxidation of metals. From these figure it is further seen that, with time there is break in linearity at longer time indicating thereby that, after some exposure there is a change in mechanism of the growth of the film. It can be noted that, the time needed for such a change to occur decreases with increasing temperature. The values of activation energies as calculated from the plot of $\ln k_p$ against $1/T$ shown in the Fig. 2 for both the stages are 76.981 kJ/mole and 99.758 kJ/mole respectively. These values are comparable to those found in literature. [6]

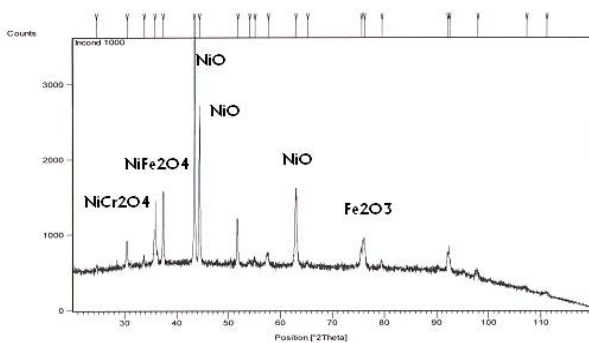


Fig.3: XRD pattern of uncoated sample at 1000°C

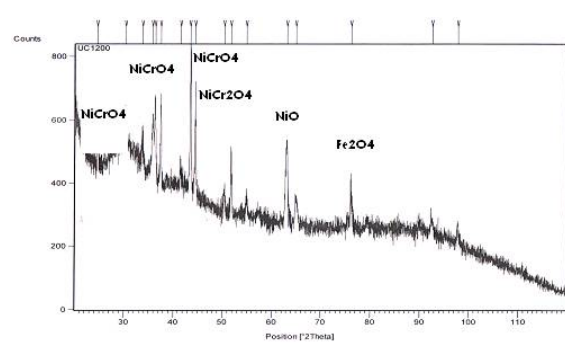


Fig.4: XRD pattern of uncoated sample at 1200°C

The XRD pattern of surface formed after 1st stage of oxidation shows presence of mainly NiO as shown in Fig. 3, while in the 2nd stage of oxidation the as shown in Fig. 4 surface comprises of phases like NiCrO₄, Fe₃O₄ and Fe₂O₃. The presence of nickel and iron in the film at a later stage of oxidation indicates complex mechanism of film growth with diffusion in the spinel structure of NiO.Cr₂O₃.

Vary low value of K_p in this region as seen from Table 2 probably suggests the mechanism of film growth with diffusion in the spinel structure of NiO.Cr₂O₃. The occurrence of nickel with the formation nickel chromate on the top surface of the uncoated alloy sample suggests outward diffusion of nickel as well during growth of the film. Although 20% chromium in the alloy is enough to carry out selective oxidation, it seems that, with time there is depletion of chromium at the interface between metal and oxide, with chromium diffusivity being less in the alloy. Because of this depletion there is a possibility of oxidation of nickel taking place simultaneously. At this stage the chromium content being not sufficiently high so as to causes selective oxidation, it acts as a dopant in the nickel oxide film and both oxide being p-type conductor, chromium with higher valency, the oxidation rate is much higher than that, of pure nickel. Some peaks in the XRD pattern shows presence of iron as well. Since there is an appreciable amount of iron in the alloy (8%) it is possible that, iron also diffuses along with chromium outwardly. Since diffusivity of the cations in the spinel is invariably less, it indicates lower value of k_p in the II-region and the activation energy is high.

With 20 % chromium in nickel chromium alloy, the selective oxidation of chromium and the film consisting exclusively of Cr₂O₃ can be expected. It is however found that, the film is of NiO in the initial stage. With time this is because oxide-containing nickel grows much faster than Cr₂O₃. With time when Ni depletion take place at the metal surface, formation of Cr₂O₃ take place by internal oxidation as well. Cr undergoes oxidation to form Cr₂O₃. This combines with NiO to form NiCr₂O₄ as is seen for the uncoated sample. This is known as transient oxidation, and has been found in many alloy system including Ni-Cr alloy Formation of islands of NiCr₂O₄ in the NiO film have been reported by many workers [7]. Once the film of NiCr₂O₄ is formed there would be steady state oxidation. This would be selective oxidation and formation of Cr₂O₃ would take place. This study is however carried out for the initial stage of oxidation and hence the formation of spinel is shown. If the oxidation would have continued for longer time there would have been a probability of Cr₂O₃ formation as reported [8].

B. BOND COATED ALLOY

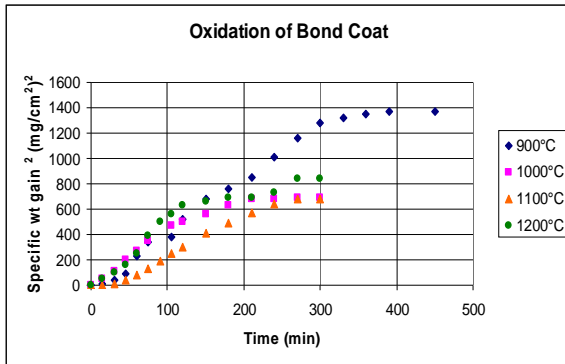


Fig.5: Plot of Square of Specific wt gain Vs Time at different temp.

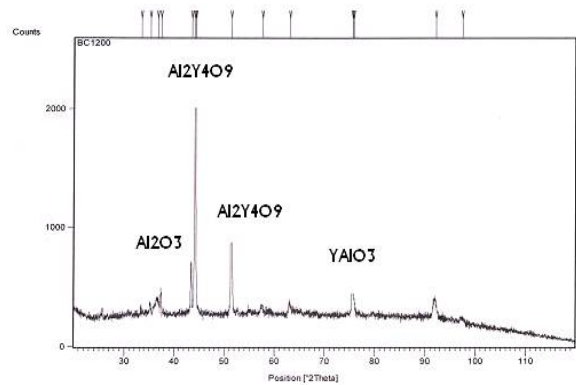


Fig.6: XRD Pattern of bondcoated sample at 1200°C

It will be seen from the Fig. 5 that, there is a linear relationship between squares of wt. gain against time, confirming the parabolic law of oxidation of metals. From these figure it is further seen that, with time there is break in linearity at longer time indicating thereby that, after some exposure there is a change in mechanism of the growth of the film. It can be noted that, the time needed for such a change to occur decreases with increasing temperature.

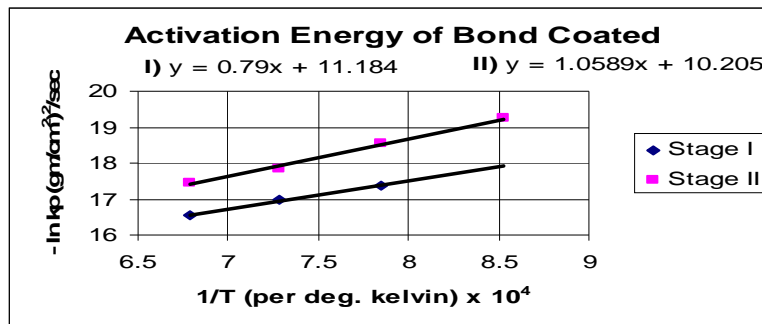


Fig.7: Plot of ln kp Vs 1/ Coated T for Bond

Fig.6 shows the XRD pattern of the surface of the base metal coated with the bond coat. Here the predominant phases present on the surface consists mainly complex oxides containing alumina and yttria. This is expected in view of the bond coat containing yttrium and aluminium. However the presence of nickel, chromium or iron in the various phases present on the surface was not seen. This indicates the protective properties of the bond coat. The alumina film offers good resistance to oxidation. This is reveled in the calculation of activation energy for oxidation. The values of activation energies as calculated from the plot of ln kp against 1/T shown in the Fig.7 for both the stages are 70.822 kJ/mole and 80.140 kJ/mole respectively. These values are comparable to those found in literature. [9]

C. YSZ COATED ALLOY

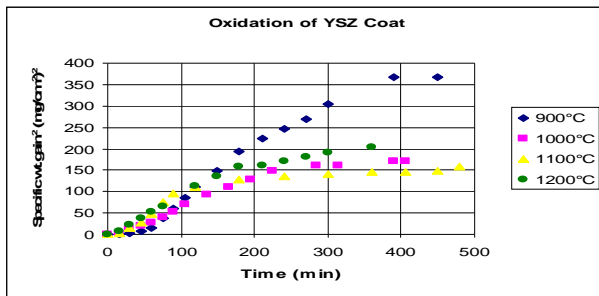


Fig.8: Plot of Square of Specific wt gain Vs Time at different temp

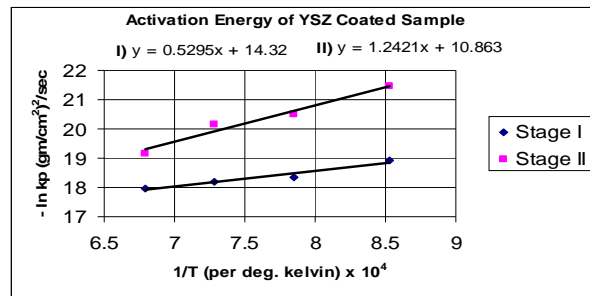


Fig.9: Plot of ln kp Vs 1/T for Bond Coated

The YSZ coating is mainly intended as a Thermal Barrier Coating and hence it is expected that, it would not improve oxidation resistance significantly. This is actually seen from the k_p values found at different temperatures. In this case, it is seen that, the activation energy as calculated by plotting $\ln k_p$ against $1/T$ as shown in Fig.9 is less than that, obtained for bond coated which in turn is less than uncoated sample for stage I. It is seen that, for stage I the activation energy decreases successively from uncoated to bond coated to YSZ coated sample while in the II stage increases in that, order. The values of activation energies as calculated from the plot of $\ln k_p$ against $1/T$ shown in the Fig.9 for both the stages are 48.036 KJ/mole and 110.853 KJ/mole respectively. These values are comparable to those found in literature [10].

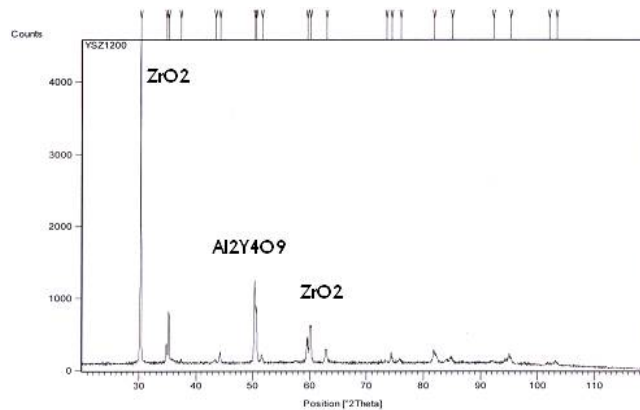


Fig. 10: XRD pattern of Bond Coated at 1200°C

In order to find out this mechanism, XRD pattern of the uncoated alloy sample oxidized at 1000°C for 2 hours was obtained. This pattern is as shown in Fig.3 shows formation of NiO predominantly. It can hence be concluded that, in the initial stage there is selective oxidation of nickel. However at later stage there is outwards diffusion of chromium as well, so that there is simultaneous oxidation nickel and chromium to form combined oxide. [8] The bond coat containing Y, Cr Al and Ni shows some solubility for oxygen. As a result there is an inward diffusion of oxygen through the bond coat. Due to high lattice diffusion of oxygen activation energy for oxidation is reduced as is seen from Table 3 In the stage I therefore before spinel formation, there is a decrease in the activation energy due to availability of oxygen. The YSZ coating is n-type conductor providing diffusivity of oxygen anions. This facilitates the oxidation and hence there is further decrease in the activation energy. The inward diffusion of oxygen in the bond coat results into oxidation of chromium in the stage II, therefore there is simultaneous oxidation of Ni and Cr resulting into spinel structure. Formation of the spinel in the product layer provides good resistance for lattice diffusion and hence the activation energy for oxidation increases considerably.

The YSZ is an n-type conductor where in the diffusivity of anions take place. The XRD pattern of the oxidized test sample of 8-YSZ is as shown in Fig.10, in this the predominant peaks shows mostly the presence of ZrO₂ and a small amount of complex oxide containing Y, Al and Zr. It therefore seems that, there is formation of alumina and this offers good resistance for the growth of the oxide film. This is reflected in increasing the activation energy for oxidation in the II stage.

Table 2: kp Values of the Test Samples

Test Sample	Activation Energy. kJ/mole	
	Region I	Region II
Uncoated	76.981	99.758
Bond Coated	70.822	83.140
8-YSZ coated	48.036	110.853

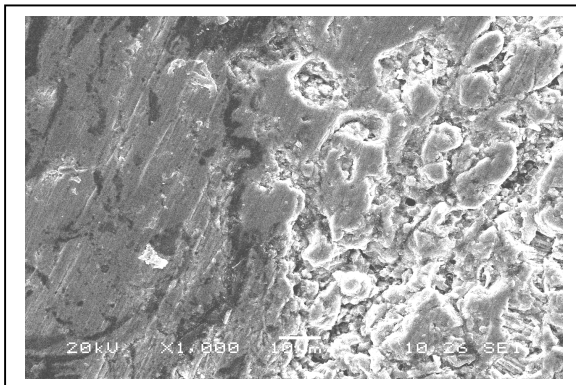


Fig.11: Cross Section SEM of Oxidized 8-YSZ sample after 6 hours at 1200°C showing clearly the thermally grown oxide.

Test sample	Temperature, °C	kp Values, g ² /cm ⁴ /s	
		Stage I	Stage II
Uncoated	900°C	6.17 x 10 ⁻⁸	3.39 x 10 ⁻⁹
	1000°C	1.16 x 10 ⁻⁷	6.53 x 10 ⁻⁹
	1100°C	1.81 x 10 ⁻⁷	1.19 x 10 ⁻⁸
	1200°C	3.16 x 10 ⁻⁷	2.26 x 10 ⁻⁸
Bond Coated	900°C	6.91 x 10 ⁻⁹	4.42 x 10 ⁻⁹
	1000°C	2.85 x 10 ⁻⁸	8.87 x 10 ⁻⁹
	1100°C	4.27 x 10 ⁻⁸	1.78 x 10 ⁻⁹
	1200°C	6.58 x 10 ⁻⁸	2.66 x 10 ⁻⁸
8-YSZ Coated	900°C	6.14 x 10 ⁻⁹	4.83 x 10 ⁻¹⁰
	1000°C	1.08 x 10 ⁻⁸	1.24 x 10 ⁻⁹
	1100°C	1.25 x 10 ⁻⁸	1.78 x 10 ⁻⁹
	1200°C	1.6 x 10 ⁻⁸	5.2 x 10 ⁻⁹

Table 3: Activation Energies of the Test Samples

III. EXPERIMENTAL RESULTS

It will be seen from forgoing discussion that, oxidation resistance of the base metal is important. Oxidation resistance in the initial stage may be due to formation of nickel oxide and at a temperature. Application of bond coat does improve the oxidation resistance and YSZ as a TBC. However the oxidation studies of the later stage the formation of nickel chromate (NiCrO₄) indicates outward diffusion of chromium as well as. This can be considered as undesirable as there can be tendency for hexavalent chromium oxide formation which is volatile at this base metal are more important

IV. CONCLUSION

1. In the case of Ni-Cr alloy there is transient oxidation in the initial stage due to which there is oxidation of nickel and formation of nickel chromate. Therefore on oxidation the surface shows presence of nickel chromate.

2. Due to bond coat there is increase in oxidation resistance. This can be attributed to the formation of Al_2O_3 . This in turns forms complex oxides with yttrium. Due to spinel structure of these complex oxides the diffusivity and hence oxidation rate is considerably reduced.
3. The TBC being n-type conductor provides oxygen at the TBC- bond coat interface. Al_2O_3 also being n-type conductor. The activation energy needed for oxidation is less. However, with formation of Al_2O_3 and other complex oxides, the activation energy required for oxidation is increased. The XRD of YSZ coated sample on oxidation however shows presence of only ZrO_2 . The Presence of Al_2O_3 and other complex oxides in the inner scale need conformation

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