

1

Efficacy of thermal barrier coated superalloy used in turbines

A. K. RAY, B. GOSWAMI¹, S. B. KUMAR² and D. K. DAS³

National Metallurgical Laboratory (Council of Scientific and Industrial Research (CSIR), Jamshedpur-831 007, India

¹R.V.S. College of Engineering and Technology, Jamshedpur-831012, India

²National Institute of Foundry and Forge Technology, Ranchi.-834003, India

³Defence Metallurgical Research laboratory, Hyderabad-500 058, India

Abstract : *The life of thermal barrier coating prior to spallation is dominated by micro cracking in both the thermally grown oxide and the yttria stabilized zirconia top coat. The damage generated by this microcracking is expected to be a primary life-limiting factor. High temperature force controlled fatigue testing of thermal barrier coated (TBC), bond coated only and bare Superni C263 superalloy, employed for manufacturing the combustion chamber of aero turbines, were conducted in air. Additionally, several accelerated creep tests on the TBC coated and on the bare Superni C263 alloy were carried out in air. Results revealed that both TBC and bond coated substrate had higher endurance limits than the base alloy, while the opposite*

was found for high stress, low cyclic life times. At high stress, the premature failure for these two materials is possibly due to high stress crack initiation/growth in the TBC/bond coat layers. Oxidation is the cause of the reduced life of the bare substrate as compared to the coated substrate while fatigue and creep experiments are carried out in an oxidizing environment. During 800°C fatigue, the bare specimens behave differently from the coated specimens, but both the bond coated only and bond coat + TBC specimens seem to exhibit very similar results that are within experimental scatter. Possibly during creep, coarsening of the grains and the γ precipitates and also the decomposition of carbides at the grain boundaries of the bare substrate gradually degrade the properties of the alloy when exposed to elevated temperatures for extended periods of time. Delamination of bond coat, oxidation of the substrate and spallation of the ceramic layer were evident at very high fatigue and creep stresses. Lateral cracks that grow in the ceramic layer parallel to the stress axis were responsible for spallation of the top coat (TBC) at very high fatigue stress, whereas at low creep stress, spallation of the top coat was due to growth of alumina scale (of thickness $>3\mu\text{m}$) at the top coat (TBC)/bond coat interface.

Key words : Thermal barrier coating; Fatigue; Superalloy; Bond coat; Substrate endurance; Stress; Crack growth; Creep; Transgranular; Intergranular; Oxidation; Spallation.

INTRODUCTION

Ceramic thermal-barrier coatings (TBCs) have received increasing attention for gas-turbine engine applications. Durability issues for TBCs under high-temperature, cyclic conditions are still of major concern, especially as future engine temperatures increase. In the global scenario, both industry and academia are actively pursuing research on evaluating the lifetime and thermomechanical behavior of superalloys with ceramic thermal

barrier coatings (TBCs), which are candidate materials for various components such as turbine blades, vanes, combustors, etc. These components generally are subjected to high mechanical stresses and aggressive environments^[1-24]. The advantages of using TBCs include increased fuel efficiency by allowing higher gas temperatures and improved durability and reliability from lower component temperatures. The ceramic TBCs provide an increase in the thermal inertia of the turbine components, and therefore a reduction of the severe thermal temperature gradients during heating and cooling^[1,8]. It was established that under conditions simulating jet engine applications^[4,5], one significant contributor to TBC failure is spalling from the oxidation of the bond coat, and many studies have concentrated on the time to spalling as a function of heat flux^[6-9] and as functions of surface stresses and crack tip opening^[9]. Analysis of life data indicates that cyclic thermal loading and thermal exposure play synergistic roles in controlling the spallation life of the coating^[17]. Studies on effects of yttrium, aluminum and chromium concentrations in bond coatings on the performance of zirconia--yttria thermal barriers revealed that without yttrium in the bond coatings, the zirconia coatings failed very rapidly. Increasing concentrations of chromium and aluminum in the Ni-Cr-Al-Y bond coatings increased the total coating lifetimes^[18]. This effect was not as great as that due to yttrium. Increased bond coating thickness was also found to increase the lifetimes^[18] and it was found^[18] that the thermal fatigue characteristics increased with decrease of the maximum principal residual stress of the top coat and the thickness of oxidation layer of the bond coat. Ceramic sintering and creep, bond-coat oxidation, the effects of thermal cycling, and their relevance to coating-life prediction are some of the critical issues surrounding TBCs^[19]. Experimental testing techniques have been developed^[19] to characterize these TBC properties on CMSX-4 substrate and to investigate the failure mechanisms of the coatings. Emphasis is placed on the dynamic

changes of the coating thermal conductivity and elastic modulus, fatigue and creep interactions, and resulting failure mechanisms during simulated engine tests^[19]. In actual practice there are situations when the surface of the combustor also bulges, due to violation of the operational stress conditions, which is a clear indication of creep damage^[2]. In such a situation, the accelerated creep data becomes important.

The aim of the present work is to estimate the life of the thermal barrier coated Superni C263 alloy under fatigue and accelerated creep conditions, which is mostly employed for manufacturing the combustion chamber of aero turbines, for its better endurance limit, efficiency and serviceability.

EXPERIMENTAL

Substrate and test sample geometry

Hot rolled Superni C-263 Ni base superalloy bar stock (Table.1) was the substrate material for the TBCs. The alloy had been solution treated (heated to 1150°C for two and a half hours and water quenched), aged for 8 h at 800°C and air cooled which lead to non-textured gamma' strengthened polycrystalline alloy with ~195 µm diameter grains containing intragranular as well as intergranular carbides^[14, 15]. Dog bone shape and flat tensile test samples with nominal dimensions of 3 mm thickness by 4 mm width and a gauge length of 35 mm were machined from hot rolled and heat treated Superni C263 bar, where the gage length was parallel to the longitudinal and rolling direction of the bar.

Table 1 : Chemical analysis of the substrate (Superni C263 alloy).

Material	Elements (wt%)						
	Cr	Co	Mo	Ti	Al	C	Ni
Superni C263 alloy (substrate)	20	20	6.0	3.0	0.5	0.6	Balance

Generation of TBCs

A Ni22Co17Cr12.5Al0.6Y type metallic undercoat/bond coat was first applied by plasma spraying to ensure the bonding and adherence of ceramic TBC to the substrate. Thereafter, zirconia-based TBC (stabilized with 8 wt% yttria) was plasma sprayed on the bond coat. Before initiation of the plasma spray, the substrate was treated through reverse transferred arc sputtering to remove any traces of oxide that may have formed during preheat to 250°C for coating. The coating thickness

Table 2 : Spray parameters for top coat (TBC) and bond coat

I. Plasma spray parameters for top coat (TBC) on the bond coat		
Plasma gas : 9MB		
Gas mixture (Argon and Hydrogen)	Pressure, MPa	Gas flow rate SCFM
Argon	0.689	80
Hydrogen	0.552	13
Arc current : 800 Amps Arc voltage : 100 Volts Spray distance : 102 mm		
II. Plasma spray parameters for bond coat (Ni22Co17Cr12.5Al0.6Y type) on substrate (Superni C-263 alloy)		
Plasma gas: SG 100		
Gas mixture (Argon and Helium)	Pressure, MPa	Gas flow rate SCFM
Argon	0.296	10
Helium	0.827	50
Arc current : 609 Amps Arc voltage : 115 Volts Spray distance : 63 mm		

was maintained by computer-controlled gun and part motion. The plasma gas for the TBC as well as for the bond coat was Metco 7 MB (mixture of Ar/H₂). Typical parameters for the TBC had a gun-substrate distance of 100 mm at a chamber of 30-60 torr (0.004-0.008 MPa), the gun operating at 80 kW with powder feed rate of around 4 kg/h. In case of the bond coat, the gun operated at 70 kW and the gun-substrate distance was 63 mm. The bond coat, as well as the ceramic layer were deposited by plasma spraying on all the four sides of the flat tensile specimens for fatigue and creep tests. The spray parameters are collated in Table.2.

Force- controlled fatigue tests at high temperature

The fatigue behavior in this investigation was studied under a high cycle and load (force) - controlled tension-tension mode at a temperature of 800°C in air, which is the desired metal temperature of the combustion chambers which invariably operate at stress levels below the yield strength and are only associated with elastic strain. Uncoated, bond coated only and TBC samples were fatigue tested, where the stresses on the bond coated only and TBC specimens were based solely on the cross sectional area of the superalloy substrate. The 800°C peak fatigue stress levels were chosen to vary from 220 MPa (50% of the yield strength of the Superalloy C-263^[14-16]) to 380 MPa (90% of yield strength) in ~40 MPa increments steps and the minimum stress corresponded to a stress ratio, R=0.1. At least two specimens were tested at each stress level for each material condition.

All the tests were performed in air on a servohydraulic (MTS-810), 50T capacity machine fitted with a 3 zone PID controlled furnace. The test temperature was monitored by Pt-Rd type thermocouples, tied at the gauge length portion of the specimen where there was no coating. Prior to the test, initially a low

sinusoidal wave pattern frequency was first applied which was gradually increased to 35 Hz for the duration of testing. All the test procedures were based on ASIM E 466-82^[25], where the load on the specimen was continuously monitored by an oscilloscope.

Accelerated stress rupture tests

Accelerated stress rupture tests as per ASTM 139/83 specification were carried out in constant load Mayes creep testing machines, in the range of 550-850°C, and in the stress range of 135 -700 MPa, for the substrate as well as for the coated specimens under identical stress and temperature. The test temperature was monitored by Pt-Rd type thermocouples, tied at the gauge length portion of the specimen. The thermocouples were tied in the same manner as were tied for the fatigue specimens. The temperature was controlled within $\pm 2^\circ\text{C}$ of the set temperature. The test was commenced only after one hour of soaking to ensure that the specimen attained the required temperature. The stress levels at each temperature were selected in such a way as to obtain rupture within a reasonable span of time^[15]. The stress rupture data have been plotted in terms of stress Vs LMP (Larson Miller Parameter).

Regression analysis of stress rupture data for the substrate material has been carried out using a standard software package, in order to evaluate its long term 1000 hour rupture strength.

$$\text{Larson- Miller Parameter (LMP)} = T (15 + \log t_r) = a_0 + a_1(\log S) + a_2 (\log S)^2 + \dots + a_m (\log S)^m \quad \dots (1)$$

Where T = Absolute Temperature in K , t_r = Rupture time in hours, S = Rupture strength in MPa , m = Order of polynomial.

a_0 , a_1 , a_2 & a_m are polynomial constants.

The ruptured creep and fatigue samples were examined in the JSM 840A SEM (Scanning Electron Microscope) to record the microfractographic details.

Metallographic examination

Bond coated only and TBC samples were polished and the thicknesses of the ceramic layer as well as that of the bond coat were measured by optical microscopy. All the samples were polished by standard metallographic technique and by using a final polishing step with 0.1 μm diamond paste. The surface was finally etched with 20% HNO_3 , 10% HCl , 20% distilled water and 50% fresh glacial acetic acid for 30 seconds and cleaned with acetone and dried, to reveal the grain boundaries and precipitation in the matrix. The precipitates in the substrate as well as in the diffused zone after the bond coat were analyzed using EDS (Energy Dispersive Spectroscopy) facility attached to JSM 840A SEM (Scanning Electron Microscope). Several failed samples were metallographically sectioned and examined to study the behavior of the TBC during fatigue and creep.

RESULTS AND DISCUSSION

Optical metallography of as-fabricated TBC coated superalloy samples revealed that the ceramic layer and the bond coat were 290 μm and $\sim 100 \mu\text{m}$ thick respectively (see Fig.1a). The ceramic layer had approximately 15 % porosity which is normally desired^[1,2]. The bond coated specimens also had a 100 μm thick Ni 22Co17Cr12.5Al0.6Y layer which contained pores^[14-16]. The substrate (Superni C-263 alloy) in its aged condition showed carbides precipitates within the grains as well as on the grain boundaries^[2], (Fig.1b).

At 800°C, fatigue testing of the TBC and bond coated specimens and uncoated Superni C-263 (Fig. 2 & Table.3), revealed that the life of the TBC and bond coated samples at high stresses ($> 300 \text{ MPa}$), low cyclic lifetimes is lower than

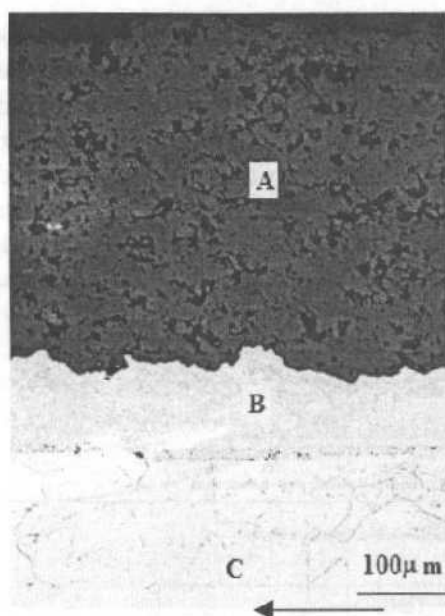
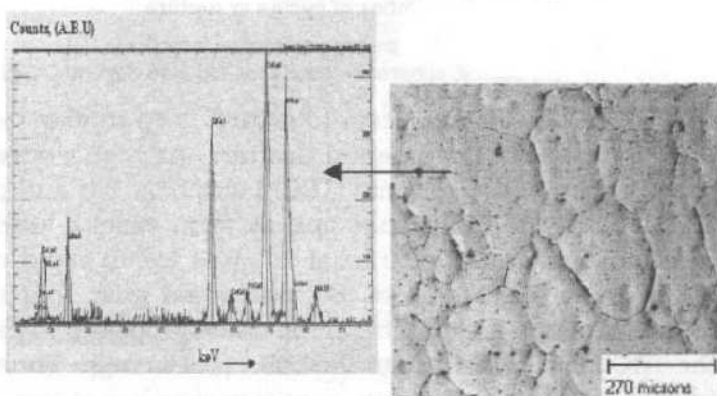


Fig.1(a) : Typical light optical photomicrograph of the thermal barrier coated Superni C263 alloy. A-TBC, B - Bond Coat, C - Substrate (Superni C263 alloy). The width of the TBC (ceramic coating- 8wt% yttria stabilized zirconia) is ~290 μm and that of the bond coat is around 100 μm .



1(b) : Light optical photomicrograph of the substrate (Superni C263 alloy).

that of the uncoated superalloy. However at about 275 MPa (Fig. 2), the TBC composite reaches its endurance limit^[14], where the fatigue stress to rupture becomes asymptotic with respect to number of cycles, which is substantially higher than the 220 MPa of the substrate. The bond coated superalloy also has an apparent higher endurance limit than the bare alloy. During fatigue, both the bond coated only and bond

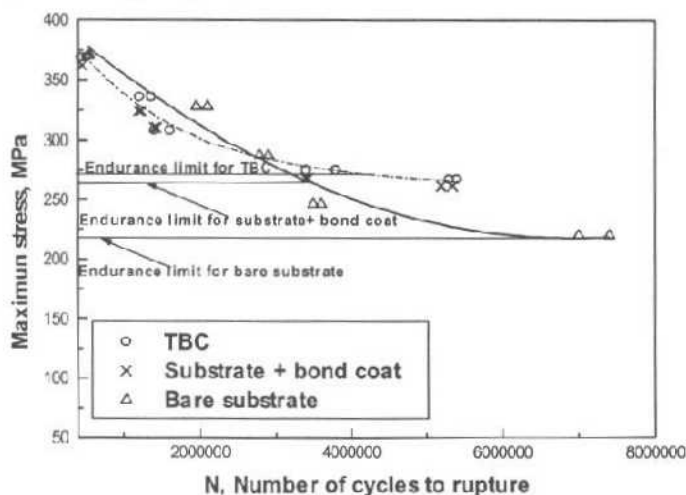


Fig. 2 : Maximum fatigue stress as a function of cycles to failure at 800°C for TBC coated, substrate + bond coat and bare Superni C-263.

coat + TBC specimens seem to exhibit very similar results that are within experimental scatter. At higher stresses microcracks in the ceramic (TBC) layer (Fig. 3a) and pores (Fig. 3b) in the bond coat join to form cracks, and the resultant generation of triaxial stresses led to rapid crack growth into the substrate. So, one could infer that when fatigue stresses are very high, the crack propagation rate in the TBC layer as well as in the bond coat is high. Thus, the fatigue life of the composite specimen was low at very high fatigue stresses. This mechanism has been extensively

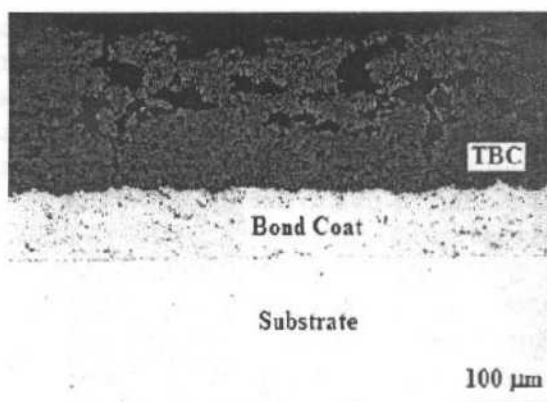


Fig. 3 : (a) Light optical cross section of 800°C fatigue failed TBC coated sample along the thickness - gage length axis far away from the failure site, tested at 336 MPa for 120,3254 cycles. Arrow indicates that several pre-existing microcracks and pores in the coating join to form fatigue cracks.

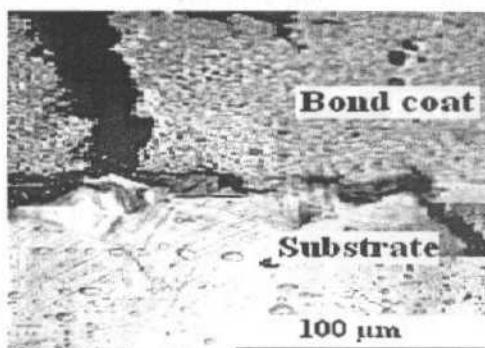


Fig. 3(b) : Optical micrograph of bond coated sample near to the rupture end along the thickness - gage length axis, that failed at 457026 cycles, during high cycle fatigue at 370 MPa/800°C. A part of the bond coat appears to be delaminated from the substrate before the crack penetrates vertically into the substrate.

documented as a failure mode occurring in many TBC coated Ni-base superalloy systems^[20-24]. It was found that this failure mode occurred owing to Ni-Co-Cr-Al-Y bond coat cracking and crack propagation into the substrate^[24].

Oxidation of surface connected cracks is likely the cause of the reduced endurance limit of the bare superalloy at intermediate stresses between 275 and 247 MPa at 800°C, as compared to either coated substrate while fatigue testing is carried out in an oxidizing environment such as air. Below 225 MPa oxidation might not be a problem for the bare superalloy, as specimens tested at ~50% YS (220 MPa) only failed at greater than 70,000,00 cycles. Such behavior is comparable to a room temperature force-controlled fatigue life for Superalloy C-263 of about 107 cycles at 200 MPa^[26]. Evidence of crack initiation in the ceramic TBC leads to decreased fatigue lifetimes during cycling under high stresses.

For low cycle, high stress lifetimes the unprotected superalloy was stronger, possible due to early crack formation and growth in the bond coat/TBC layers. It was observed from Fig. 3c that during fatigue at low stress (247 MPa), there

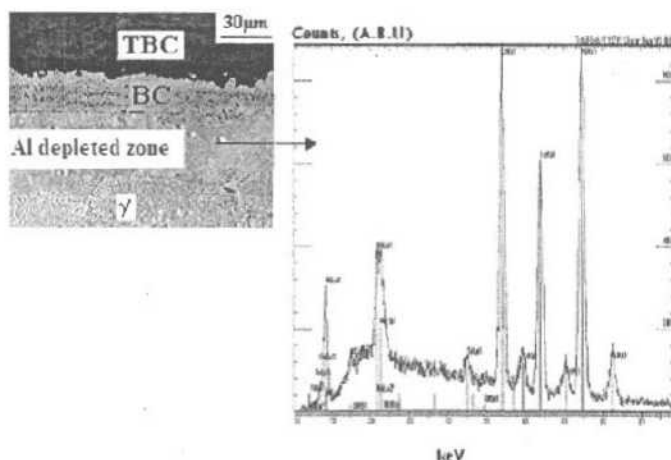


Fig. 3(c) : Light optical cross section of 800 °C fatigue failed TBC coated sample along the thickness - gage length axis away from the failure site, which ruptured at intermediate stress (247 MPa) after 5,400, 107cycles. BC indicates bond coat.

was interdiffusion of Al^[1,8,9,13,20,28] from the bond coat to the substrate and possibly also at the TBC/ bond coat interface, as revealed in the microstructure of the TBC failed specimen which failed after 54, 00107 cycles at 247 MPa during 800°C fatigue test in air. This interdiffusion of Al, possibly resulted in an Al depleted zone (Fig. 3c) at the bond coat/substrate interface with formation of rich γ phase in the substrate, as was also observed by earlier investigators in oxidized TBC specimens^[1,8,9,13,20,27]. Formation of rich β -Ni3Al phase (γ phase) in the substrate would result in overall strengthening of the TBC composite specimens, although the bond coat/substrate interface was relatively weak^[1,8-9,13]. Probably a similar phenomenon has had occurred during 800°C fatigue testing of the TBC samples in air, in the present investigation too (see Fig. 3c). This phenomenon was also clearly observed during accelerated creep of the TBC specimens at low stress level, which would be discussed while highlighting the reason for spallation of the top coat of these TBCs during creep at low stress. Previous bend tests^[1,8,9,13] on TBC coated substrates (Inconel 617 and CMSX-4 alloys) with Ni-18Cr-12Al-0.5Y type of bond coat, at 800°C has indicated that the oxidized TBC specimens showed a substantial higher bending strength compared to the bare substrate and non oxidized TBC specimens due to interdiffusion of Al from the bond coat to the substrate and also to the TBC/bond coat interface. It was observed^[1,6, 9,13] that a part of the Al from the bond coat diffuses into the substrate to form β -Ni3Al phase in the substrate, and a part of it diffuses at the interface of TBC/bond coat layer to form an Al₂O₃ layer of 2 μ m thickness at the interface of TBC/bond coat in case of oxidized thermal barrier coated CMSX-4 alloy^[1,8, 9,13]. Nevertheless, the bare substrate was found to be severely oxidized when it ruptured after 7000293 cycles at 220 MPa during 800°C fatigue tests (Fig. 3d). So one could

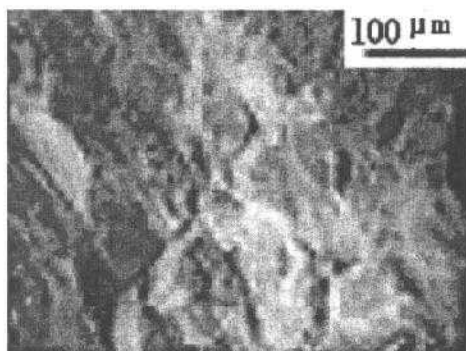


Fig. 3(d) : Fractograph of the bare substrate that ruptured in force-controlled fatigue test at 800°C, after 7,000, 293 at 220 MPa.

infer that oxidation is also the likely cause of reduced life of the bare substrate as compared to the coated substrate while fatigue testing is carried out in an oxidizing environment. This agrees well with the observation made by previous investigators^[15,29,30].

In the present investigation it was observed that during 800°C fatigue, the bare specimens behave differently from the coated specimens, but both the bond coated only and bond coat +TBC specimens seem to exhibit very similar results that are within experimental scatter (Fig. 2 and Table 3). The TBC layer however, is very brittle and its strength is negligible^[1,8,28]. Plasma spraying induces an extremely large thermal gradient onto the surface of the specimen that is being coated. Under many instances, residual stresses might form within the deposited coating and substrate. As the nature of the residual stresses might influence the fatigue behavior of the specimens, measurement of residual stresses in each layer of the composite was essential^[28]. After generation of the TBC specimens in the present investigation, residual stresses measured on the top coat, bond coat and on the substrate, using an AST portable stress analyzer from the peak shift in the $\text{Sin}^2\psi$ method, have been reported and discussed

Table 3 : High cycle 800°C fatigue data of TBC, bond coated and bare substrate specimens

Sl. No	No of cycles for TBC specimen	Stress of TBC specimen, MPa	No of cycles for bond coated specimen	Stress of bond coated specimen, MPa	No of cycles for bare substrate specimen	Stress of bare substrate specimen, MPa
1	450098	369	457026	362	532084	370
2	504572	369	452200	362	551230	370
3	1203254	336	1191245	324.2	1950492	328
4	1356723	336	1227123	324.2	2100642	328
5	1400064	308	1410528	310	2900763	287
6	1602870	308	1430111	310	2785025	287
7	3400361	275	3392145	268	3600730	246
8	3793195	275	3429033	268	3492178	246
9	5299435	247	5190375	261.4	7000293	220
10	5400107	247	5345782	261.4	7400147	220

elsewhere^[28]. Data collected for x-ray stress work and XRD pattern on each layer of the composite sample over a range of 2θ range 132 to 135° using CrK α (30kV/5mA) radiation showed that the nature of residual stress present in the plasma sprayed TBC (top coat) was tensile, whereas that in the bond coat as well as in the substrate was compressive (see Fig.4). Each measurement was taken using four tilt angles ($\Psi = 0$ to 45°). Due to the presence of residual stress, σ_p , there would be a peak shift Δd in the x-ray diffraction curve. The peak shift was used for calculation of σ_p , from the following equation^[28]:

$$\sigma_p = E \Delta d / (1 + \gamma) \sin^2 \Psi \quad \dots (2)$$

Where E is the Young's modulus and γ is the Poisson's ratio. The values of E, γ and the respective diffracting planes of each layer

(TBC, bond coat and substrate) are reported and discussed elsewhere^[26]. Fig. 4 shows that the magnitude of the residual stress in the TBC was of the order of 12 to 34 MPa which is negligible^[28]. Therefore, residual stresses in the top coat of this order of magnitude would have negligible effect or influence on the fatigue behaviour of the TBC specimens. Below the TBC (top coat) layer, is the bond coat and it had compressive residual stresses^[28]. The bond coat was first deposited on the substrate by plasma spraying and on its top, the TBC was generated by plasma spraying. So,

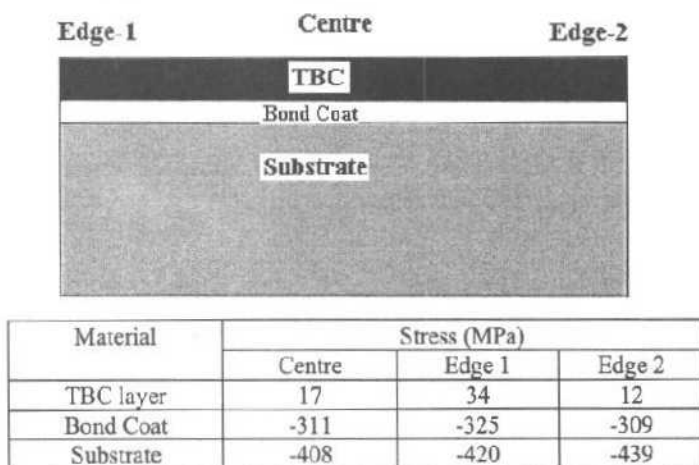


Fig. 4 : Schematic of the TBC coated substrate indicating the locations and nature of residual stresses^[28].

whatever tensile residual stresses would have been introduced in the bond coat due to the plasma spraying technique, they would have been relieved (by stress relieving)^[28] due to the deposition of the ceramic layer (TBC or top coat) on the top of the bond coat. Therefore, finally after the generation of TBC specimen, the top coat or TBC layer showed tensile residual stresses and the bond coat revealed compressive stress, which is due to the deposition of ceramic layer (TBC) on the bond coat. The substrate also revealed compressive residual stresses. Compressive residual stresses are

beneficial, as they would increase the fatigue life of the entire composite specimens comprising of three layers. It should be noted that the term compressive in the present case is used only in a relative sense from the negative sign in order to delineate from the tensile residual stresses present in the ceramic layer.

Scanning electron fractographs of 800°C failed fatigue samples of the bare Superni C-263 indicated that fracture occurred in an intergranular mode with cleavage facets at high fatigue stresses (Fig. 5a), but took place transgranularly with ductile dimples at low stress (Fig. 5b) while intermediate stress levels yielded a mixed mode of failure (Fig. 5c). Fatigue striations were also revealed in ruptured samples at low stresses of the bare substrate (Fig. 5b),

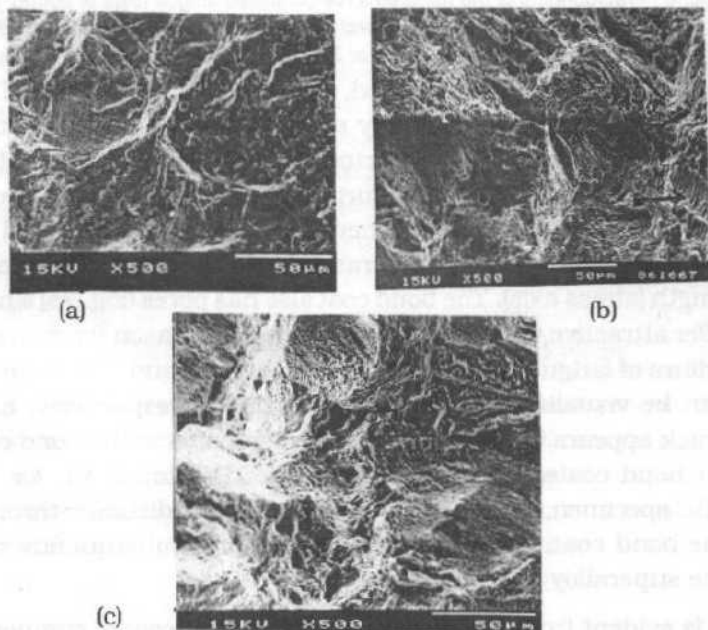


Fig. 5 : Fractographs of the ruptured force-controlled fatigue tests at 800 °C, for the bare Superni C263 (a) 370 MPa for 551,230 cycles to failure , (b) 220 MPa for 7,400, 147 cycles to failure and (c) 287 MPa for 2,785,025 cycles to failure.

indicated by arrow. Examination of the long life time coated fatigue specimens after 800°C testing revealed ductile transgranular failure for the bond coated only specimen^[16] tested at 260 MPa (Fig. 6a) and the TBC coated specimen at 275 MPa^[16] (Fig. 6b).

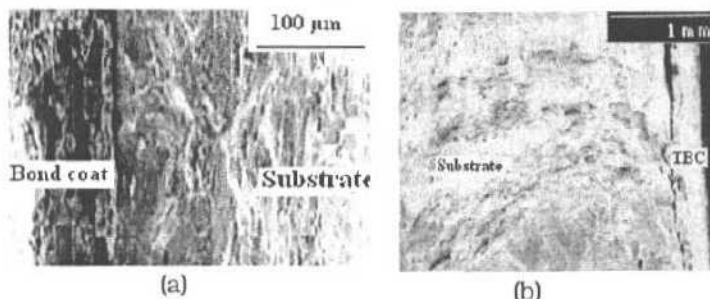


Fig. 6 : Fractographs of the ruptured force-controlled fatigue tests at 800°C [16] for the coated Superalloy C263 (a) bond coat only at 261.4 MPa for 5,345,782 cycles to failure and (b) TBC coated at 275 MPa for 3,793,195 cycles to failure.

Several metallurgical polished, unetched sections of the TBC coated and bond coated only specimens were examined and are revealed in Fig. 7(a&b). Factors leading to potential spallation of the ceramic TBC (Fig. 7b), during fatigue testing at high stress, can be seen in Fig. 7(a), where lateral cracks (indicated by arrows) are growing in the ceramic layer parallel to the sample length (stress axis). The bond coat also has pores (Fig. 7a) which offer attractive sinks for crack blunting. The reason for eventual failure of fatigue tested bond coated samples and TBC samples can be visualized in Fig. 7(c) and Fig. 7(d) respectively, as a crack appears to be initiated from micropores in the bond coat for bond coated specimen and in the TBC (top coat) for the TBC specimen, which then propagates perpendicularly through the bond coat, as indicated by arrow, and subsequently into the superalloy substrate.

It is evident from Fig. 8, that the life of TBC coated composite under accelerated creep is substantially high in terms of rupture time, compared to that of the substrate material. This is

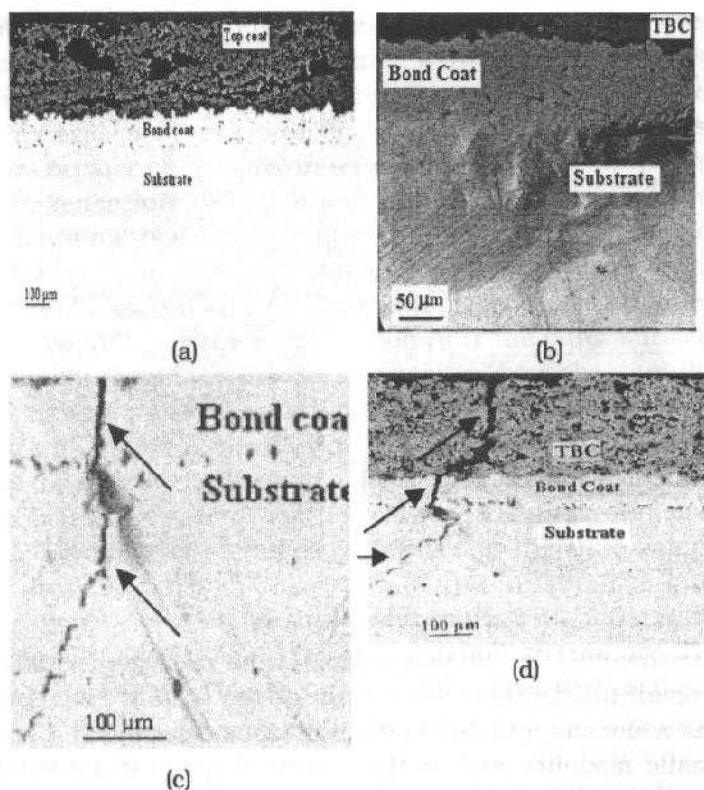


Fig. 7 : Light optical cross sections of 800 °C failed samples along the thickness - gage length axis (a) away from the failure site for the TBC coated tested at 369 MPa for 504,572 cycles; (b) adjacent to the ruptured end for the TBC coated tested at 369 MPa for 504,572 cycles. Spallation of the top coat and deformation twins are revealed in the substrate, (c) bond coated only tested at 268 MPa for 3,429,033 cycles, and (d) away from the failure site, revealing crack propagation in the TBC as well as in bond coat. The sample was tested at 308 MPa for 1400064 cycles.. Arrow indicates the cracks.

because oxidation is known to reduce the creep life time of bare metals as compared to coated metals^[15,29,30] or unexposed metals^[31] when tested in air/ oxidizing environment. The phase precipitation and phase stability^[32] and conventional creep behavior of the substrate alloy are reported and discussed

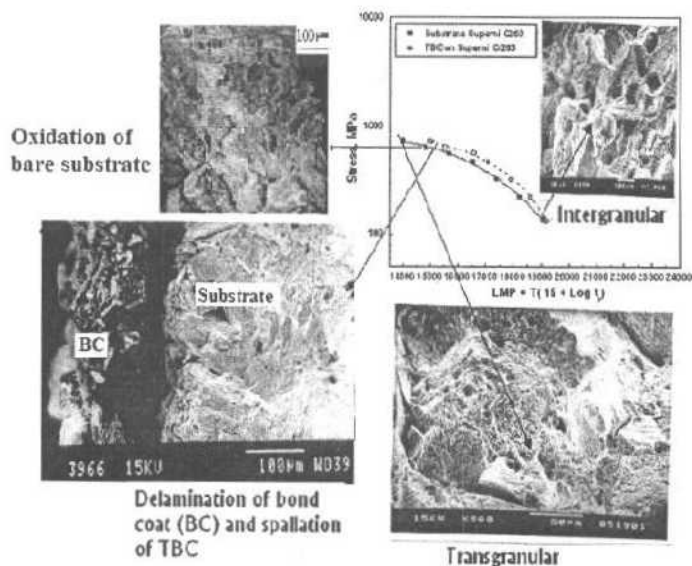


Fig. 8 : Variation of stress with LMP.

elsewhere^[31,33-36]. While considering the relative mechanical properties of the superalloy and the overlay coating^[1,8], the latter has a low strength due to the numerous defects and a lower elastic modulus, and so the system alloy + coating can be considered as a composite in which the load bearing contribution of the ceramic coating is negligible. However from tensile test data at high temperatures of the bond coated Superalloy C-263^[14], it was found that the bond coat was ductile above 650°C; thus the bond coat should be possible of bearing load at 800°C. Previous compressive testing of overlay coated substrates, such as Ni-18Cr-12Al-0.5Y, at 800°C has indicated that a creep stress ~25 MPa would result in a creep rate of 10^{-7} s^{-1} , while a creep stress ~300 MPa was required to deform the substrate at 10^{-3} s^{-1} ^[37]. Thus partial support of the applied loads by the bond coat alloy could result in apparent strengthening^[37].

In the present investigation, long term rupture strengths were estimated with best fitted curves for first and second order polynomials in equation -1. For different orders of the polynomial, the average sum square error (ASSE) was estimated from the following equation:

$$ASSE = \sum (Y_{\text{experimental}} - Y_{\text{estimated}})^2 / n \quad \dots (3)$$

where n is the number of data points. The first order polynomial was selected for estimation of rupture strength as there was no significant change in the average sum square error for higher orders. The polynomial constants from regression analysis are shown in Table 4. In accelerated creep, the mode of fracture in the substrate at very high stresses was transgranular (Fig. 8). This is because at high stresses, due to strain-rate dependence of creep^[36] and since the metal

Table 4 : Polynomial constants from regression analysis.

Type of material	Order of polynomial	Standard deviation	a_0	a_1
Superni C263 alloy (substrate)	m=1, C = 15	99.11931	2.02×10^4	-8.52
TBC coated substrate	m=1, C = 15	99.053	2.03×10^4	-7.23

is creeping, the stresses within it tend to be lower than that for ductile fracture and the nucleation of voids is postponed to larger strains. The flow can be stabilized and void coalescence is postponed. So, the fracture in this limited range of creep is transgranular. However at lower stresses a transition from transgranular to intergranular fracture occurs (see Fig. 8) because of the fact that within this region, grain-boundary sliding becomes prevalent and wedge cracks and voids grow on the grain boundaries^[38] lying roughly normal to the tensile axis. Al depleted zones were also observed^[1,8,9,13,20,27]

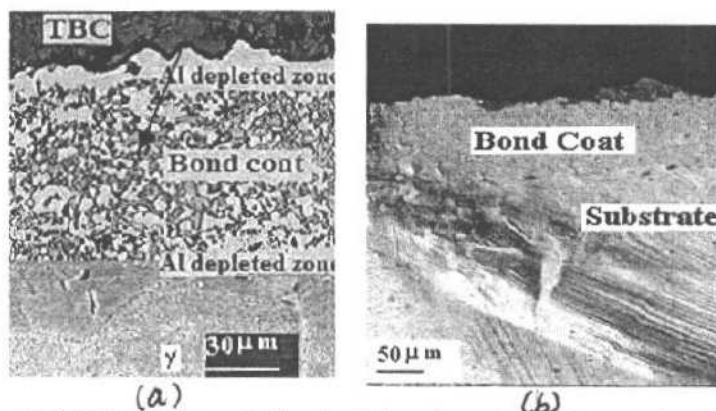


Fig.9 : (a) Optical micrograph of bond coated sample near to the rupture end along the thickness - gage length axis, that failed during creep at 220 MPa/ 850°C. Al depleted zone was observed at TBC/ bond coat and bond coat/substrate interfaces due to diffusion of Al from bond coat to substrate and at the interface of bond coat /TBC layer. Precipitation of rich γ phase is revealed in the substrate. Arrow indicates the growth of Al_2O_3 layer of thickness $>3 \mu\text{m}$, which eventually leads of spallation of the top coat (TBC layer) as shown in (b).

at the bond coat/substrate and TBC/ bond coat interfaces during creep at low stress (Fig. 9a). The interdiffusion between the bond coat and the substrate is beneficial considering the bond strength, especially in the case of arc ion plated MCrAlY coatings. The Al diffuses to the top coat/bond coat interface to be oxidized at the interface. The oxidation at the top coat/bond coat interface invariably has an adverse effect on the intactness of the TBCs. Although the alumina layer is essential for better adherence of the top coat onto the bond coat, but if it the thickness of the alumina layer is $>3\mu\text{m}$, then the top coat never remains intact. This would therefore, lead to spallation of the top coat from the bond and hence the TBC composite would fail^[27,2930].

It was concluded^[22], that due to the selective oxidation of Al in the NiCoCrAlY bond coat and a Ni_3Al film on the surface of the bond coat, an Al_2O_3 layer develops between the bond

coat and the transition layer^[22]. The major consequence of TBC oxidation is detachment of the top coat from the bond coat leading to spallation of the top coat (see Fig. 8b), due to a thermally grown oxide scale (TGO) which is a continuous Al_2O_3 scale growth of $2\mu\text{m}$ thickness, at the top coat /bond coat interface (see Fig. 8a). Previous study on failure modes in plasma-sprayed thermal barrier coatings^[23] revealed that as the TGO thickened, cracking occurred at the bond-coat/TGO interface, and in some instances cracking also occurred at the TGO/top-coat interface, but primarily at crests of bond-coat undulations. The bond-coat-TGO separation resulted in 'layering' of the TGO at crests due to enhanced TGO thickening^[23] in those regions. In the troughs of bond-coat undulations, cracking occurred within the top-coat when the TGO was thick. Thus, the primary failure modes in these TBCs^[23] were: (i) cracking of the bond-coat/TGO interface; (ii) cracking within the top-coat; and (iii) linking of these microcracks by fracture of the TGO, leading to spallation of the top coat.

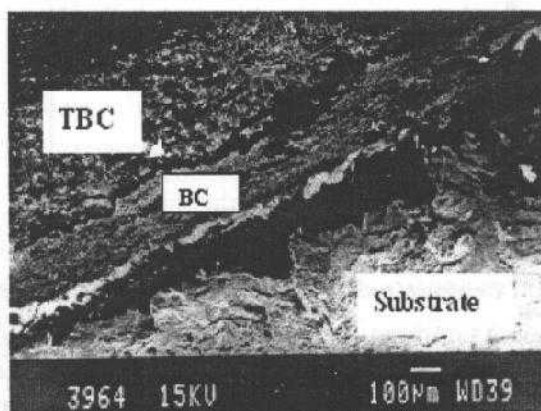


Fig. 10 : Fractograph revealing delamination of TBC layer from bond coat and that of bond coat from substrate observed during creep at high creep stress , 710 MPa /850°C.

The 15% porosity in the topcoat is normally favorable. However, the porous structure of the bond coat is detrimental to the oxidation resistance of the bond coat particularly during creep, in case that a continuous alumina scale growth is formed on the surface of the bond coat or at the top coat/bond coat interface, which eventually leads to spallation of the top coat even at low creep stress (Fig. 9a & 9b).

Delamination of the bond coat, oxidation of the substrate and spallation of the TBC at very high stresses during creep were evident (Fig. 10 and Fig. 8). Fig. 11 reveals the variation of rupture strength, S of the substrate material in the temperature range of 550° to 800°C, for various rupture times. It is clear from Fig.11, that the estimated 100 -10,000 hr rupture strengths at various temperatures showed a decreasing trend

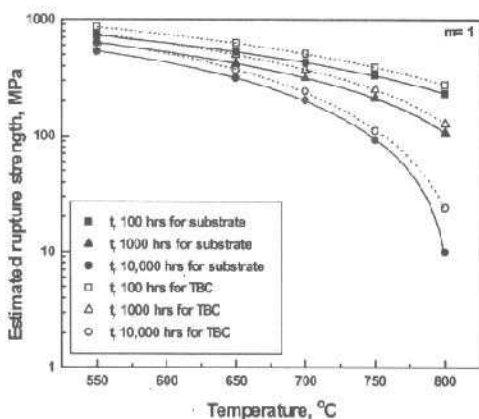


Fig. 11 : Variation of estimated rupture strength with temperature

with increasing temperature, which is a common phenomenon observed in creep resistant materials. Microstructural study^[31] on oxidized creep specimens of the same superalloy revealed that the outer layer of oxidized specimen containing intergranular oxide^[31] and the depletion of γ' , had a considerable

damaging effect on the creep properties of superalloy C263. Prior exposure of this alloy caused both creep ductility embrittlement and a creep weakening effect, resulting in poor creep life^[31]. In the present investigation, the extent of creep cavitation in the bare superalloy C263 is clearly revealed in Fig. 12, when the bare substrate ruptured at 220 MPa/ 850°C.

For the bare substrate, the major precipitates^[32] at temperatures below 900°C were γ and η (Ni_3Ti), with the η phase starting to precipitate at the expense of γ phase after prolonged annealing. Grain boundary precipitates were mostly M_{23}C_6 and with a small fraction of MC ^[32]. Since the η formation is detrimental to the mechanical properties, the alloy is precipitation- annealed at 800°C for 8 hours to promote γ formation and it is usually used at temperatures $\leq 800^\circ\text{C}$ to avoid η formation during service^[32]. Possibly, coarsening of the grains and the γ precipitates^[32] and the decomposition of carbides at the grain boundaries gradually degrade the

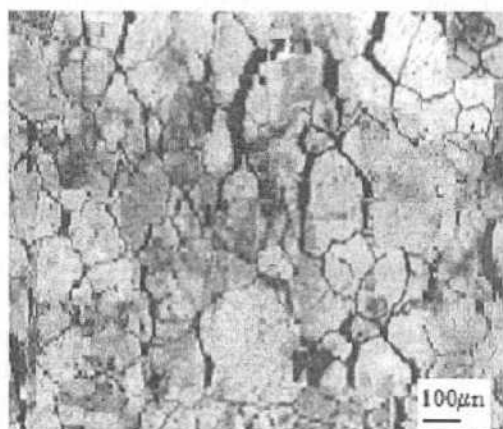


Fig.12 : Optical micrograph showing the extent of creep cavitation damage across the thickness in the creep ruptured bare superalloy C263 which ruptured at 220MPa/850°C in air. The micrograph also reveals grain coarsening and intergranular precipitation /decomposition of carbides

properties of the alloy when exposed to elevated temperatures for extended periods of time. During the period where the microstructure is transforming, the mechanical properties of the alloys continue to degrade. After prolonged exposures, however, microstructure attains a thermodynamic equilibrium and stabilizes along with the creep response of the alloy.

CONCLUSIONS

- (1) Fatigue testing of bare, bond coated only and TBC coated Superni C-263 at 800°C in air revealed that the coated materials had higher endurance limits than the bare superalloy. However for low cycle, high stress lifetimes, the unprotected superalloy was stronger, possible due to early crack formation and growth in the bond coat/TBC layers. Both the bond coated only, and bond coat + TBC specimens exhibit very similar fatigue lifetimes, that are within experimental scatter. Oxidation is likely the cause of the reduced life of the bare substrate as compared to the coated substrate while fatigue and creep experiments are carried out in an oxidizing environment. During creep, possibly coarsening of the grains and the decomposition of carbides at the grain boundaries of the bare substrate gradually degrade the properties of the alloy when exposed to elevated temperatures for extended periods of time.
- (2) The mode of fracture in the substrate at very high fatigue stresses was intergranular whereas that at low fatigue stresses was transgranular. Whereas, for creep the reverse is true^[39]. The life of thermal barrier coating prior to spallation is dominated by microcracking in both the thermally grown oxide and the yttria stabilized zirconia top coat. The damage generated by this microcracking is expected to be a primary life limiting factor. Spallation of the ceramic (TBC) layer was evident at very high fatigue

stress where lateral cracks grow in the ceramic layer parallel to the stress axis and for creep, even at low creep stress, due to the continuous growth of alumina scale of thickness $>3\mu\text{m}$ at the top coat (TBC)/bond coat interface.

ACKNOWLEDGEMENT

The authors are grateful to AR&DB (Aeronautical Research and Development Board) for sanctioning and funding this project and to Prof. S.P. Mehrota-Director, NML Jamshedpur for his permission to publish this manuscript. The authors are grateful to M/s D.P. Engineering Corporation-Jamshedpur, for their assistance in fabrication of the samples and to Mrs Ameeta Dhawan for her assistance in bibliography.

REFERENCES

1. A. K. Ray, Inter. J. Turbo & Jet Engines. 17(2000) 1.
2. A. K. Ray and D. K. Das, Materials letters. 60 [2006] 3019.
3. W. J. Brindley and R. A. Miller, Surf. Coat. Technol. 43-44 (1990) 446.
4. C. H. Liebert, and R. A. Miller, Ind. Eng. Chem. Prod., Res. Dev. 12 (1984) 334.
5. K. Kokini, C. D. Choules and Y. R. Takeuchi, J. Therm. Spray. Tech. (JTTEE) ASM International. 6 (1997) 43.
6. L. Lelait, S. C. AlperineDiot and M. Mevrel, Mater. Sci. Eng A. 121 (1989) 475.
7. K. Kokini, and Y. R. Takeuchi, Mater. Sci. Eng. A. 189 (1994) 301.
8. K. M. Godiwalla, N. Roy, S. Chaudhuri and A. K. Ray, Inter. J. Turbo & Jet Engines. 18 (2001).77.
9. N. Roy, K. M. Godiwalla, S. Chaudhuri and A. K. Ray, High Temperature Materials and Processes. 20 (2001) 103.
10. C. C. Chiu and E. D. Case, Mater. Sci. Eng A. 132 (1991) 39.
11. D. R. J. Owen, and E. Hinton, Finite Elements in Plasticity, Pineridge Pres Limited, Swansea, U.K (1980).

12. W. Brandle, H. J Grabke., D. Toma and J. J. Krueger, *Surf.coat.Technol.* 41(1996) 87.
13. N. Roy, K. M. Godiwalla , E.S. Dwarakadasa, A.K. Ray, *Scripta Met.* 7(2004) 739.
14. A. K. Ray, D. K. Das , B. Venkataraman, P. K. Roy, B. Goswami, N. Roy, S. K. Das, N. Parida, S. Tarafder, S. Chaudhuri and R. N. Ghosh, *Mat. Sci. Eng. A.* 405(2005) 194.
15. A. K Ray, E. S. Dwarakadasa , N. Roy, B. Dash., D. K. Das, B. Goswami, S. K. Sahay, D. Sanyal and R. N. Ghosh, *High Temp Mater and Processes.* 25 (3) (2006)109
16. A. K. Ray, E. S. Dwarakadasa , D. K. Das , V. R. Ranganath, B. Goswami, J. K. Sahu and J. D. Whittenberger, *Mat. Sci. Eng A*, 448 (2007)294.
17. T. A. Cruse, S. E. Stewart and M. Ortiz, *J. Eng. Gas Turbines Power (Trans. ASME)*, 110 (4) (1988) 610.
18. S. Stecura, *Thin Solid Films.* 73 (2) (1980) 481.
19. D. Zhu and R. A. Miller, R. A., *MRS Bulletin.* 25 (7) (2000) 43.
20. S. D. Peteves, E. Tzimas,; I. Mulleijans, J. Bressers and W. Stamm, *Acta Materialia.* 48 (18-19) (2000) 4699.
21. A. Peichl, T. Beck, and O. Vohringer, *Surf. coat.Technol.* 162 (2/3) (2003)113.
22. H. Guo, S. Gong, C. Zhou and H. Xu, *Surf.coat.Technol.* 148 (2-3) (2001) 110.
23. K. W. Schlichting, N. P. Padture, E. H. Jordan and M. Gell, *Mat.Sci. Eng-A.* 342 (1-2) (2003) 120.
24. Y. H. Zhang, P. J. Withers, M. D. Fox, D. M. Knowles, *Mat. Sci.. Technol.* 15 (9) (1999) 1031.
25. Standard practice for conducting amplitude axial fatigue tests of metallic materials, Designation:E 466-82, Annual Book of ASTM standards (1994) pp 465.
26. B. Gupta, et.al, *Aerospace materials with general metallurgy for engineers*, Vol II New Delhi, India (1996).
27. W. Brandle, H.J. Grabke, D.Toma and J. Krueger, *Surf.Coat.Technol.* 86-87 (1996) 41.

28. A. K. Ray. et.al., Material Characterization, 57 (3) (2006) 199.
29. K. H. Stern, "Metallurgical and ceramic protective coatings" Chapman and Hall(1996) P4.
30. T. Focke and D. S. Lashmore D. S., Scripta Metall, 27 (1992) 651.
31. S. Srivivas, M. C. Pandey and D. M. R. Taplin , Eng.Failure Analysis. 21(3) (1995) 191.
32. J. C. Zhao, V. Ravikumar and A. M. Beltran, Metall and Mat Trans A. 32A (2001) 1271.
33. A. Manonukul, et al, Inter. J.of Plasticity. 21 (2005) 1.
34. A. Manonukul, et al, Acta Mat. 50 (2002) 2917.
35. Y. H. Zhang, et al, Mat Sci and Technol. 18 (2002) 917.
36. Y. H. Zhang, et al, Mat Sci and Technol. 17 (2001) 1551.
37. W.J. Brindley and J.D. Whittenberger, Mat. Sci. Eng A. 163 (1993) 33.
38. Dieter George E., Mechanical Metallurgy (Mc Graw Hill Publishers, Metric Edition, 1986).