ISSN(Online) : 2319 - 8753
ISSN (Print) : 2347 - 6710

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 5, May 2015

Zirconia and Nickel Based Thermal Barrier Coating

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ABSTRACT: This research project focuses on thermal properties of Zirconium and nickel based materials. Zirconium ceramics with its low thermal conductivity, good adhesion properties with bond coat material which are nickel based alloys acts as a good thermal barrier coating material. Also, the focus on optimizing thermal barrier coating structure using Comsol Multiphysics 4.3 Software. Thermal barrier coating increase the engine operating temperatures hence increasing the efficiency and performance. Samples of Zirconium, Oxidised zirconium (zirconia) are prepared and thermal properties are found out using laser flash technique DLF-1200 equipment. Results show that oxidised zirconium with its very low thermal conductivity in the range 3.5-4.5 W/m.K for temperatures 25 degree C – 1000 degree C, is the suitable material to coat engine system components like piston, cylinder head, and exhaust manifold. Nickel super alloys used are Haynes 718,230,625 and nickel N out of which nickel n and nickel 718 have the lowest thermal conductivity ranging 5-22 W/m.K. More research should be done on the characteristic surface properties of oxidised zirconia to evaluate it as a thermal barrier coating material. Simulations are done for different values of thickness for bond coat and top coat of a thermal barrier coating and maximum and minimum von misses stress is calculated. Results show that optimized thickness for a thermal barrier coating is 60µm for bond coat and 120µm for the top coat which has the minimum stress value.

KEYWORDS: TBC- thermal barrier coating, DLF- direct laser flash, YSZ yittria stabilized zirconia

I. MATERIALS AND METHODS

Materials used in the research project are: Zirconium, Zirconium oxide (Zirconia) (prepared by heating in furnace at 973K and for 22hours, Nickel 718, N, 230, 625.
Laser detection technique is used to experimentally find out the thermal properties of the material DLF-1200 equipment. For optimizing the thermal barrier coating structure, Comsol Multiphysics software 4.3 is used.

II. INTRODUCTION

1.1. Objective:

To determine thermal properties of Zirconium materials and nickel alloys which can used as a thermal barrier coating materials in engine system components like piston, cylinder head, exhaust manifold and optimize coating structure by temperature and stress analysis using Comsol Multiphysics software.

1.2. Background:

Thermal barrier coatings (TBC) have gathered interests of researchers and industry for over fifty years now. TBC are highly advanced thermally insulating materials that are applied to surface of metal components to provide insulation from elevated temperatures. Thermal barrier coatings are used regularly in automotive (diesel engines) and aviation (gas turbines engines) industry. Hejwowski et al (2002) showed that TBCs minimize heat loss, allows for higher operating temperatures, and extends the machine components' life by reducing oxidation and thermal fatigue. For diesel engine parts, more than 55% of the energy produced during combustion is removed by cooling water/air and through exhaust gas. In order to save energy, it is important to protect the hot parts by thermally insulation. Thermal insulation reduces in-cylinder heat transfer from the engine combustion chamber. Containment of heat also contributes to increase in cylinder work and offers higher exact temperature for energy recovery. TBC can be applied to piston,

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International Journal of Innovative Research in Science, Engineering and Technology

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cylinder head, exhaust manifold, valve springs, brake callipers, brake rotors, intercoolers, oil pumps, connecting rods, crank shafts and just about any other part that sees heat or motion.

TBCs usually comprise four layers: the metal substrate, metallic bond coat, thermally grown oxide, and ceramic topcoat. To date, two methods are used for application on TBC on metal components used in automotive industry. One of them, diffusivity, is the process in which the deposited mass is diffused with substrate to form a uniform composition. Examples of diffusion technique include pack cementation and chemical vapour deposition. The other method, overlay coating, involves deposition of materials at just the surface of the material. Overall coating process can be accomplished by thermal spray process such as plasma sprayed metal matrix composite coating, physical vapour deposition process, magnetron sputtering coating, Ni-dispersion coating and electric arc wire spray coating. The most widely used process TBC in automotive industry is the plasma spray technique. Properties of materials used in ceramic coating materials for TBC are shown in Table 1 (adapted from Yilmaz et al., 2010).

Several ceramic materials such as zirconium oxide, titanium oxide, chromium oxide and mullite have been investigated as in-cylinder engine coatings. Currently, yittria stabilised Zirconia (YSZ) is the "state of the art" material for ceramic topcoat and NiCrAloy is used as the bond coat material.

The design of TBC for automotive applications is aimed to protect the metallic surface from prolonged elevated temperature and allow for efficient heat management. Design variables for TBC include number and thickness of layers and the type of material being used. The thickness of top coating material can range from 0.05 to 2 mm. The primary challenges posed by thermal barrier coatings within engine environments stem from their durability. Due to their low coefficients of thermal expansion in comparison to the metallic substrates upon which they are applied, ceramic TBCs are prone to cracking, spalling and eventual failure resulting from the cyclic thermal stresses created by the temperature differential between the coating and the substrate. The increased surface temperatures in a TBC-coated combustion chamber may also result in the degradation of engine lubricants, while decreasing the volumetric efficiency of the engine due to heating of the intake charge.

1.3. Motivation:

Strive to increase engine efficiency and fuel economy has led to more research on materials. TBC materials have been shown to improve efficiency of diesel engines by 50% due to effective exhaust heat management. Initiatives by United States Council for Automotive Research LLC (USCAR) such as Freedom CAR, Fuel Partnership and U.S. DRIVE (Driving Research and Innovation for Vehicle efficiency and Energy sustainability), suggest that novel TBC materials will be required in future. The highly durable and cost effective propertise of YSZ make it the super-star TBC material for engine components with current operating temperatures. However, with advancements in research and in anticipation of still higher operating temperatures for next generation automotives, TBCs that will be capable of operating at higher temperatures and for longer times than YSZ will be required.

III. EXPERIMENTS

Thermal conductivity for Zirconium, Zirconium oxide, Nickel super alloy inconel718, Inconel 625, Inconel 230 and Nickel N were determined using the formula mentioned in section 7.2. The dimensions of all the material samples were 12.7x12.7 mm and 1.5mm-2mm thickness. Oxide and hydride of Zirconium were prepared as described below.

Preparation of oxide:Zirconium sample was heated in air for 22 hours and at 700 oC. The sample was cooed to room temperature and presence of oxide layer was confirmed by visual inspection.

Standard operating procedure for the direct laser flash equipment:

Before starting the test:

1. Make sure argon gas is available for purging.
2. Get the liquid nitrogen and fill the detector chamber till it is full.
3. Check the level of oil in the vacuum pump.

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International Journal of Innovative Research in Science, Engineering and Technology

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4. Measure the thickness of the test sample.

5. Prepare the sample using the graphite spray and make sure you remove graphite from the sides of the samples by cleaning using ethanol.

6. The size of the sample is 12.7 x 12.7 mm (square with a thickness up to 6 mm) or a cylindrical sample with a diameter of 12.7 mm or 25.4 mm.

Operating equipment

1. Switch on the equipment by turning on the power button (available at the back of the equipment).
2. Insert the sample in the sample holder and place it in the equipment.
3. Turn on the vacuum pump till we attain the pressure of around 150 mTorr.
4. Once this pressure is attained then switch off the vacuum pump.
5. Open the delivery knob of the argon cylinder and adjust the gas inlet pressure to 40-50 psi.
6. Open the purge gas inlet on the equipment.
7. Now the pressure indicator would rise and adjust the purge gas flow adjustor clockwise to attain a pressure of 500 Torr.
8. At this pressure you could see bubbles forming at the purge gas outlet.
9. Again adjust the purge gas flow adjustor needle anti-clockwise such that you will have a smooth flow of bubbles (around 2-3 bubbles per second).
10. Once the flow of gas is adjusted then turn on the water cooler.
11. Make sure all the green LED's at the back of the instrument is bright.
12. Rest of the procedure is controlled by the software.

Three consecutive laser shots were done for each sample and the average values for thermal diffusivity and conductivity were obtained

Design considerations:

The model studies the temperature profile and stress analysis with the help of Comsol Multiphysics software 4.3. The software is used for the design and simulation of thermal barrier coating structure with different bond coat and top coat thickness.

Materials and properties taken into consideration:

Material	**Temp (℃)**	**E(Gpa)**	**ρ(Kg/m^3)**	**α(10^-6/K)**	**ν**	**k(W/m.K)**	**C(J/Kg.K)**
Nickel 718 super alloy	25	200	8220	14.4	0.3	5.3	431
	400	179	8220	14.4	0.3	9.34	524
	800	149	8220	14.4	0.3	22.4	627
NiCrAloy	25	225	7320	14	0.3	4.3	501
	400	186	7320	24	0.3	6.4	592
	800	147	7320	47	0.3	10.2	781
Zirconia ZrO2	25	53	4400	7.2	0.25	4.1	500
	400	52	4400	9.4	0.25	4.2	576
	800	46	4400	16	0.25	4.4	637

Table1: properties of the materials used for simulations:

Assumptions:

1. A circular disk specimen and a 2-D axisymmetric view is considered.

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International Journal of Innovative Research in Science, Engineering and Technology

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2. All layers are homogeneous and isotropic, there are no defects in each layer, and the interfaces between the two adjacent layers are flat without defects or wave characteristic.
3. The upper surface of the top coat transfers heat with air by convection, the side surface is adiabatic, and heat radiation was not considered in the current simulation.
4. The creep and plastic deformation of all layers are negligible and were not taken into account
5. The ceramic layer was assumed to be linear elastic; only when the stress is beyond the yield stress, crack can be initiated in the coating, and the coating begins to fail.

An axial symmetric problem was chosen in order to reduce the data processing time and to improve the computational efficiency
Physics used:
The simulation uses the physics of structural mechanics – thermal stress in the thermal barrier coating structure.
Study type is Time-dependent.

Convective cooling:
The heat transfer that is attributed to the convection between the plasma jet and the super alloy substrate was also included in the current model. The convective coefficient between the outer surfaces of the coating samples and the static air was assumed to be 100W/(m2 K).
The temperature of the atmosphere was set at 27 ◦C, and the cooling time was assumed to be 1200s. Initial temperature for the substrate boundary is given as 475k, 800k for different simulations.

Meshing: Finite element size is used for meshing for all the simulations.

Design description:
Thermal barrier coating structure with different thickness of the bond coat and top coat are designed and simulated. Von misses stress and temperature profile is studied. Thickness with minimum stress is optimized.

Drawings		Thickness(µm)	
	Substrate	Bond coat	Top coat
Model 1	3200	50	100
Model 2	3200	60	120
Model 3	3200	75	150
Model 4	3200	100	200

Table 2: Dimensions of the model

IV. Experimental results

Thermal diffusivity, conductivity and specificity were determined using the laser flash equipment. Before starting with the experimental samples, stainless steel samples were tested in the equipment to obtain reference standards. Stainless steel was also used as a quality control. The values for thermal diffusivity and conductivity for stainless steel (reference sample) are shown:

Segment	Temperature (°C)	Thermal conductivity(W/m.K)	Thermal diffusivity(cm^2/s)
1	45	13.8128	0.0402
2	97	13.9774	0.0438
3	196	14.3856	0.0458
4	295	14.7265	0.0474
5	396	15.0286	0.0494

6	494	15.4358	0.0515
7	596	15.958	0.0534
8	693	16.2826	0.0546
9	797	16.8264	0.055
10	894	17.6258	0.0569
11	997	18.6582	0.0572

Table 3: thermal properties of stainless steel

The values obtained for stainless steel samples met the equipment benchmarks.
Following are the thermal diffusivity, thermal conductivity and specific heat values obtained by laser flash technique for different zirconium based materials (top coat material) and nickel super alloy materials(substrate material)

1. Zirconium:

Segment	Temperature(℃)	Thermal conductivity (W/m.K)	Thermal diffusivity (cm²/s)	Specific heat (J/(kg·K))
1	25	13.8852	0.0936	385.4162
2	97	14.7937	0.0923	416.8649
3	198	15.9093	0.0907	456.9247
4	296	15.6908	0.0903	453.927
5	394	16.2378	0.0909	467.4814
6	492	17.4158	0.0927	493.1135
7	594	17.7203	0.0959	485.9869
8	697	18.0262	0.0982	464.5837
9	795	18.3856	0.1024	479.5349
10	894	18.9138	0.1392	499.5924
11	998	19.2568	0.1436	488.538

Table4: thermal properties of zirconium.

The results showed that the thermal conductivity of zirconium does not increase much as the temperature is increased.

2. Oxidized zirconium (Zirconia): Sample oxidized for 22 hours at 700 ℃

Segment	Temperature(℃)	Thermal diffusivity (cm²/s)	Thermal conductivity ((W/(m·K))	Specific heat(J/(kg·K))
1	25	0.0359	4.5327	1468.8154
2	94	0.0339	4.1979	1494.1742
3	197	0.0308	4.0172	1631.6046
4	293	0.0286	3.7382	1719.25
5	393	0.0269	3.5859	1787.2572
6	493	0.0262	3.7065	1869.9261
7	593	0.0275	4.4388	1977.2985
8	693	0.0445	4.5832	2048.5863
9	796	0.0497	4.8393	2104.5811
10	894	0.0573	4.86583	2119.2337
11	997	0.0598	4.8995	2256.479

Table5: thermal properties of zirconia ($ZrO2$)

IJIRSET

ISSN(Online) : 2319 - 8753
ISSN (Print) : 2347 - 6710

International Journal of Innovative Research in Science, Engineering and Technology

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The results show that as the material is oxidized, the thermal conductivity is reduced by a good percentage which is ideal for a thermal barrier coating top coat.

Comparison:
The values of thermal conductivity are compared with yttria stabilized zirconia which is the current material used in the top coat of a TBC.

Thermal diffusivity:

Segment	Temperature(degree C)	Thermal diffusivity(cm^2/s)		
		Zr	ZrO2	YSZ(ref.9)
1	25	0.0936	0.0359	0.0329
2	100	0.0923	0.0339	0.0312
3	200	0.0907	0.0308	0.0295
4	300	0.0903	0.0286	0.0275
5	400	0.0909	0.0269	0.0267
6	500	0.0927	0.0262	0.0265
7	600	0.0959	0.0275	0.0315
8	700	0.0982	0.0445	0.0334
9	800	0.1024	0.0497	0.0376
10	900	0.1392	0.0573	0.0382
11	1000	0.1436	0.0598	0.0368

Table6: comparison of thermal diffusivity of materials with yttria stabilized zirconia which is currently used in the industry

The thermal diffusivity of zirconia is comparable to the diffusivity of yttria stabilized zirconia and hence can be used as a thermal barrier coating top coat material.

Thermal conductivity:

Segment	Temperature(degree C)	Thermal conductivity(W/m.K)		
		Zr	ZrO2	YSZ(ref.9)
1	50	13.8852	4.2327	3.4928
2	100	14.7937	4.1979	3.2964
3	200	15.9093	4.0172	3.1935
4	300	15.6908	3.7382	2.9457
5	400	16.2378	3.5859	3.1126
6	500	17.4158	3.7065	3.4955
7	600	17.7203	4.4388	3.7945
8	700	18.0262	4.5832	3.8492
9	800	18.3856	4.8393	3.4964
10	900	18.9138	4.8658	3.6939
11	1000	19.2568	4.8995	3.9552

Table7: comparison of thermal conductivity of materials with YSZ

The results and graph shows that the thermal conductivity of zirconia is comparable to the thermal conductivity of yttria stabilized zirconia and more research should be done on the other properties like coefficient of thermal expansion, adhesion of the material to evaluate it as a thermal barrier top coat material.

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Nickel alloys:

1. Nickel 718
2. Nickel 625
3. Nickel N
4. Nickel 230

1. Nickel 718:

Segment	Temperature(C)	Thermal diffusivity(cm^2/s)	Thermal conductivity(W/m.K)	Specific heat(J/Kg.K)
1	47	0.0286	5.6095	1370.2242
2	95	0.03	6.0467	1417.704
3	198	0.0331	7.2128	1562.5175
4	296	0.036	8.1533	1653.9052
5	395	0.0388	9.1527	1721.0273
6	494	0.0414	10.876	1917.2211
7	594	0.0363	27.2544	5480.1929
8	694	0.0344	23.2975	4942.4292
9	793	0.0349	22.7633	4395.3733
10	893	0.0369	21.4726	4142.7436
11	996	0.0372	20.6553	3956.39

Table8: thermal properties of nickel 718

2. Nickel 625:

Segment	Temperature(C)	Thermal diffusivity(cm^2/s)	Thermal conductivity(W/m.K)	Specific heat (J/Kg.K)
1	47	0.0279	8.3814	2105.1443
2	95	0.0293	8.9386	2149.5767
3	198	0.0325	10.486	2310.635
4	296	0.0355	11.506	2361.043
5	395	0.0383	12.857	2451.1282
6	494	0.0407	14.1308	2531.2615
7	594	0.0363	45.2206	9088.6826
8	694	0.0274	25.8546	6897.7261
9	793	0.0301	24.8253	6011.2461
10	893	0.0399	19.3754	3542.8538
11	996	0.0356	18.4962	3472.5735

Table9: thermal properties of nickel 625

3. Nickel N

Segment	Temperature(C)	Thermal diffusivity (cm^2/s)	Thermal conductivity(W/m.K)	Specific heat (J/Kg.K)
1	47	0.0364	6.7218	1293.4042
2	95	0.038	7.229	1341.493
3	198	0.0414	9.1205	1579.7544
4	296	0.0449	9.831	1596.0576

IJIRSET

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ISSN (Print) : 2347 - 6710

International Journal of Innovative Research in Science, Engineering and Technology

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5	395	0.0483	11.0503	1670.4789
6	494	0.0514	11.4322	1624.8695
7	594	0.0498	16.9393	2482.8499
8	694	0.0522	18.3259	2564.6882
9	793	0.05584	18.9485	2486.6943
10	893	0.05963	19.5935	2304.4934
11	996	0.05396	19.5682	2293.953

Table10: Thermal properties of nickel N

4. Nickel 230

Segment	Temperature(C)	Thermal diffusivity(cm^2/s)	Thermal conductivity(W/m.K)	Specific heat(J/Kg.K)
1	47	0.026	8.3686	2253.5637
2	95	0.0277	8.9301	2273.4834
3	198	0.0314	10.8959	2485.8101
4	296	0.0342	11.8275	2518.364
5	395	0.0376	14.0194	2723.5847
6	494	0.0402	15.4155	2796.4041
7	594	0.0413	23.8053	4203.54
8	694	0.0452	14.4438	2334.3171
9	793	0.0498	14.7846	2457.8649
10	893	0.0537	15.664	2593.8543
11	996	0.0549	15.9374	2619.8592

Table11: Thermal properties of nickel 230

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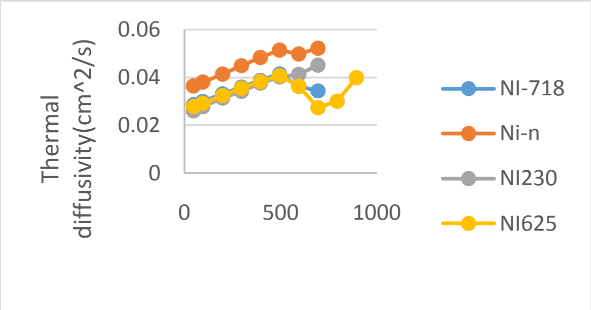
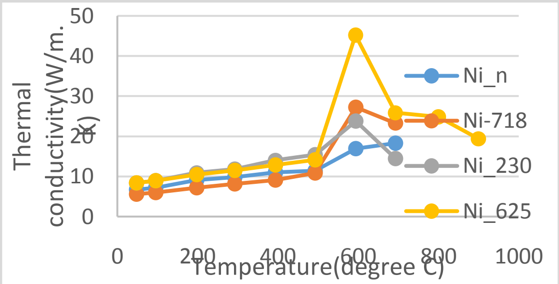
Comparison:



(a)



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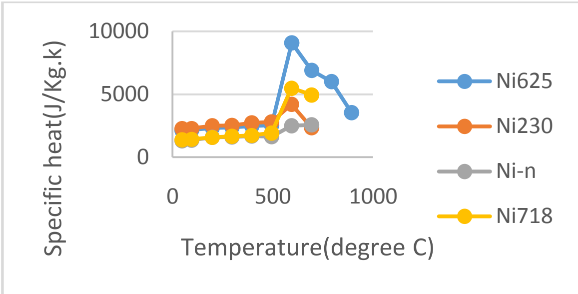
ISSN(Online) : 2319 - 8753
ISSN (Print) : 2347 - 6710

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 5, May 2015



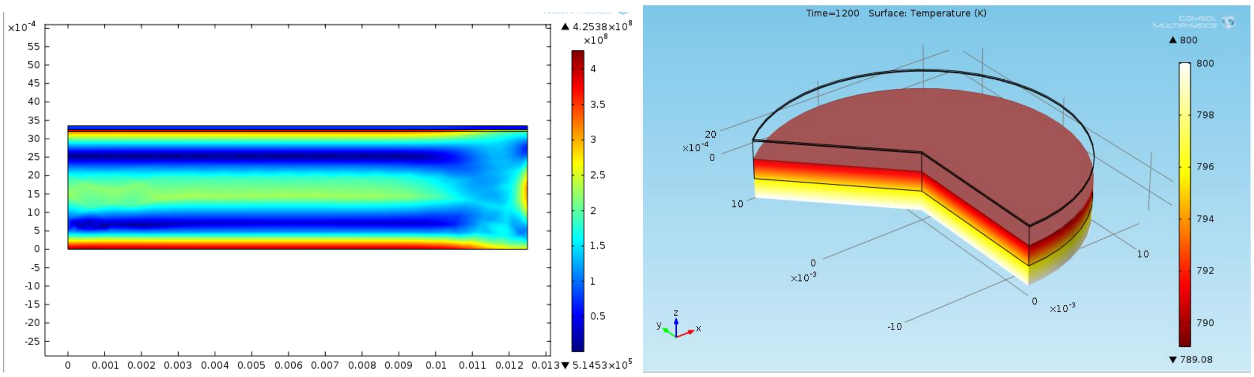
(C)

Graph (a) thermal diffusivity comparison (b) thermal conductivity comparison (c) specific heat comparison

The comparison graph shows that nickel n and nickel 718 super alloys have the lowest thermal conductivity and more studies can be done on these two materails to use them as the substrate material for a TBC.

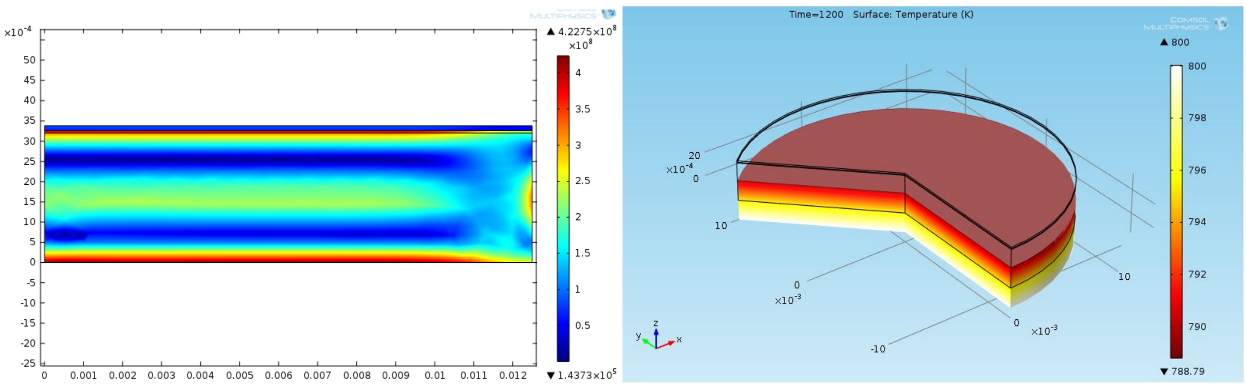
Stress and temperature analysis is done for TBC coating structure using nickel n (substrate material), NiCrAloy (bond coat) and zirconia (top coat) material properties using comsol multiphysics software and results are shown below:

Model1:



(a)

Model2:



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ISSN(Online) : 2319 - 8753
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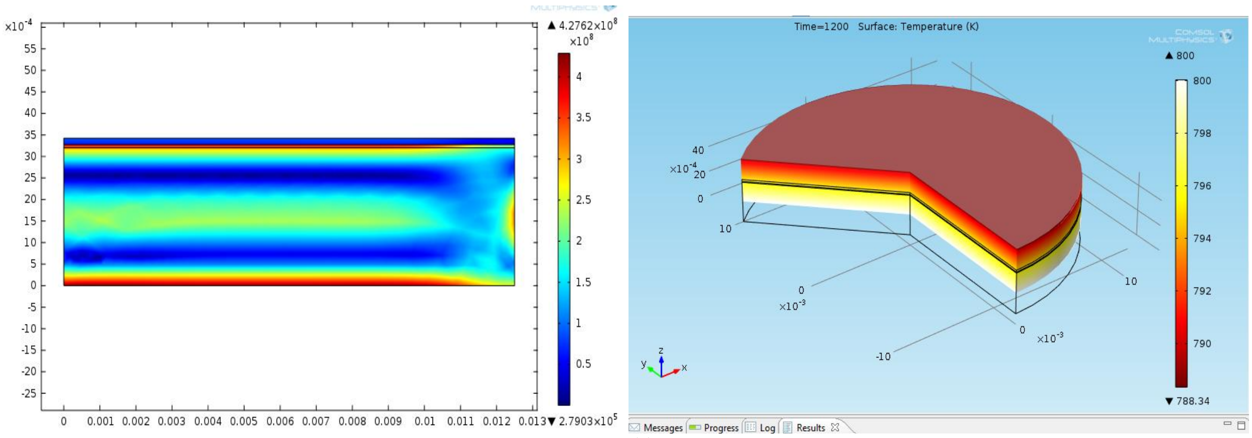
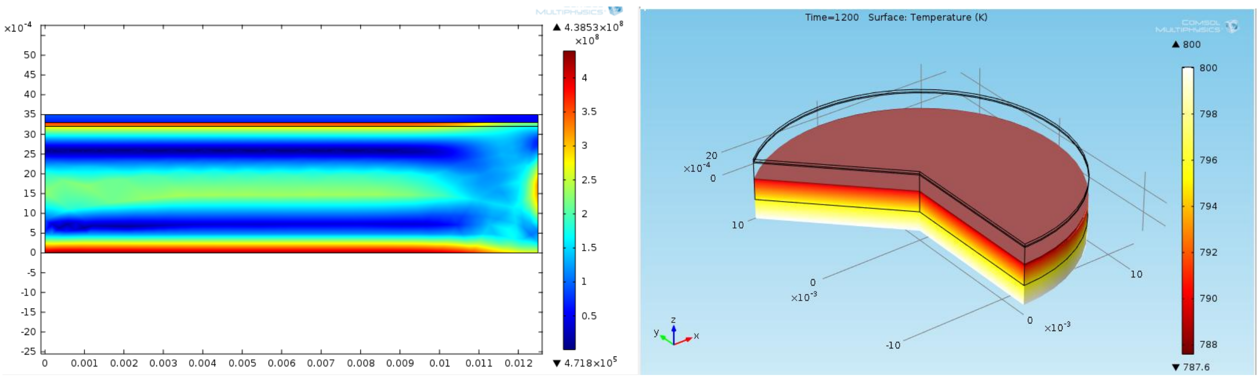
Model3:



(c)

Model4:



(d)

Fig. (a) temperature and stress analysis for model 1 (b)temperature and stress analysis for model 2 (c) temperature and stress analysis for model 3 (d) temperature and stress analysis for model 4

Model	Maximum stress(N/m^2)	Minimum stress(N/m^2)	Temperature at top coat boundary(K)
1	4.2538 X 10^8	5.1453 X 10^5	789.08
2	4.2275 X 10^8	1.4373 X 10^5	788.79
3	4.2762 X 10^8	2.7903 X 10^5	788.34
4	4.3853 X 10^8	4.718 X 10^5	787.6

Table12: results for the von misses stress and temperature simulation

V. CONCLUSION

Thermal properties and stress analysis for different materials and coating structure thickness is done. Results show that zirconia with its lowest thermal conductivity is the effective top coat material for a thermal barrier coating and nickel super alloy 718, N are the suitable substrate materials. Also, the optimised thickness for the bond coat and top coat material is 60µm and 120µm. Minimum stress value 1.4373 X 10^5 N/m^2. More research should be conducted on

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International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 5, May 2015

characteristic properties, adhesion properties of Zirconia and nickel based alloys to evaluate them as a thermal barrier coating.

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