FAILURE MECHANISMS OF THERMAL BARRIER COATINGS IN INTERNAL COMBUSTION ENGINES AND IMPROVEMENTS

Adnan Parlak, Sakıp Köksal, Aslan Çoban, İsmet Çevik

***Abstract*- Mechanical properties of high performance ceramics have been improved to the point where their use in heat engines is possible. The high temperature strength and low thermal expansion properties of high performance ceramics offer an advantage over metals in the development of non-water cooling engine. However, because hard environment in diesel engine combustion chamber, solving the problem of durability of TBC is important. Durability of thermal barrier coatings(TBC) is limited by two main failure mechanisms: Thermal expansion mismatch between bond coat and top coat and bond coat oxidation. Both of these can cause failure of the ceramic top coat. Developments of recent years show that bond coats with higher oxidation resistance tend to have better coating system cyclic lives.**

Key words: TBC, Oxidation, Thermal Expansion Mismatch

***Özet*- Dizel motorlarında, Termal bariyer amaçlı kaplamalarda(TBK) soğutma sistemine transfer edilen enerjinin azaltılması, hatta soğutma sisteminin ortadan kaldırması hedeflenmektedir. Bununla birlikte, TBK' ın dizel motorlarında maruz kaldığı şartların ağırlığı, kaplamanın dayanımı yönünden ortaya çıkan problemlerin çözümünü gerektirmektedir. Bu problemin en önemlileri ana malzeme, ara tabaka ve kaplama malzemesi arasındaki ısıl genleşme uyuşmazlığı ve oksidasyon problemidir. Araştırmalar göstermektedir ki kaplamanın oksidasyona karşı direnci arttıkça kaplamanın dayanımı önemli ölçüde artmaktadır. Bu çalışmada, TBK amaçlı olarak kullanılan seramik malzemelerde kusura neden olan mekanizmalar ve iyileştirme yöntemleri incelenmiştir.**

Anahtar Kelimeler: TBK, Oksidasyon, termal genleşme uyuşmazlığı.

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I. INTRODUCTION

It has been reported that the power and efficiency in heat engines increase with increasing combustion temperature [1, 2, 3, 4]. Design requirements and durability demands necessitate sophisticated material selection for extended service life. As a result, advanced materials such as ceramics, composites and heat-resistant super alloys have become important alternatives. At present, coating materials that resist oxidation, corrosion, erosion and wear and that provide thermal barriers have been widely used in aerospace and automotive industry [5].

In diesel engines, thermal barrier coatings were initially intended for extending service life of the components and for corrosion protection. However, recently conducted studies have aimed at reducing heat rejection to the coolants and increased engine efficiency in diesel engines [6].

Some of the important properties required of the ceramic materials used for thermal barrier applications are as follows:

- Heat resistance
- Chemical inertness
- High fracture toughness
- Low specific heat
- High compressive strength
- High thermal shock resistance
- Phase stability
- Low thermal conductivity
- Low cost
- Low modulus of elasticity
- Low thermal expansion mismatches

Typical properties required of a LHR diesel engine:

• Temperature limits (°C)	> 1800
• Fracture toughness, K_{IC}	> 8.0
• Flexural strength, MPa	> 800
• Thermal conductivity, (W/m.°C)	< 0.01
• Thermal shock resistance, °C	> 500

- Thermal expansion coefficient, ($x10^{-6}/°C$) < 10

In table 1 are listed a number of applications along with what are considered to be critical materials requirements. The only component application not specifically for the adiabatic diesel is that of wear faces or tappet/cam follower inserts. Most of the other applications require thermal shock resistance.

Partially Stabilised Zirconia (PSZ) is one of the oxides that combines the required TBC properties of low thermal conductivity, high resistance to thermal degradation, fairly good toughness and coefficient of thermal expansion (CTE) fairly close to those of most super alloys. Whitout a reasonable match in the CTE, stresses high to cause coating failure can be generated at the coating/substrate interface during even mild thermal cycling. Therefore, PSZ has been the subject of the most research for TBC applications [10, 11, 12].

Table 1 Applicability of Toughened PSZ to Engine Components (14)

Required property / Application	Strength	Compresive Strength	Fracture Toughness	Bondable to Steel	Thermal Shock Resistance	Thermal Expansion to Steel	Thermal Insulation	Low Coeff. Friction	Corrosion/Erosion resistance	Wear/Scuff Resistance
Wear faces	x	x	x	x						x
Valve seats		x			x	x			x	
Valve Guides						x	x	x		x
Cylinder Liner	x		x		x	x	x	x	x	
Precombustion Chamber					x	x			x	
Fire Deck (hot plate)	x		x		x	x	x		x	
Piston cap	x		x	x	x	x	x		x	

II. TBC FAILURES AND THEIR MECHANISMS

During plasma spray coating process, residual compressive and tensile stresses are generated that cause cracking and spalling of the coating layer. The reasons for this type of failure include followings: (a) complex interaction of grit blasted substrate surface stresses, (b) shrinkage of molten splats of bond coat metal and zirconia, (c) stresses due to temperature transients in the substrate and coating (d) thermal expansion mismatches of the materials, (e) bond coat oxidation, (f) heterogeneous heating of the substrate, (g) the geometry of the substrate. The coating thickness is the main parameter that affects the coating strength. Excessive coating thickness results in residual stresses that lead to spalling of the coating layer. In addition coating materials with high modulus of elasticity, high porosity and oxide inclusions are the other factors that degrade coating strength [7, 13].

TBC failure in the form of spalling occurs due to separation of the ceramic top coat form the bond coat in a single layer. Spalling occurs due to cracking in the top coat near and at the top coat/bond-coat interface driven by stresses attributed to oxidation of the bond coat and cyclic thermal expansion mismatch.

Cyclic life of a TBC decreases when it is exposed to environments that promote oxidation of the bond coat. Bond coat oxidation damage can reduce TBC cyclic life to only one cycle under severely oxidising conditions of high temperatures and long times in air. As reported by Brindley at al. [6], Although the oxidation of bond coat is an important degradation mechanism, it is not the only parameter affecting the bond coat degradation. They claim that, high chromium (35 wt %), low-aluminium (6 wt %), NiCrAlY bond coats show significantly better top-coat life than the NiCrAlY compositions used for overlay coatings (15-22 wt % Cr and >6 wt % Al) even though the oxidation resistance of the high chromium coatings is not as good as that provided by overlay coatings. As for the reasons for this finding, they proposed that bond coat modulus, CTE, strength or compositional effects on adhesion may be important factors in TBC life.

Cracking is initiated at interfaces due to stress concentration when the difference in the values of CTE of substrate, bond coat and top coat exceeds 30 % [15].

Mechanical degradation of TBC can results from contaminants that do not react chemically with the PSZ. Therefore, the presence of the molten condensate has little effect on the top coat while the top coat remains at high temperatures. Because the condensate freezes upon cooling during a normal thermal cycle, the frozen condensate in the pores and cracks of the coating reduces the strain tolerance of the coating and cause premature coating failure [6].

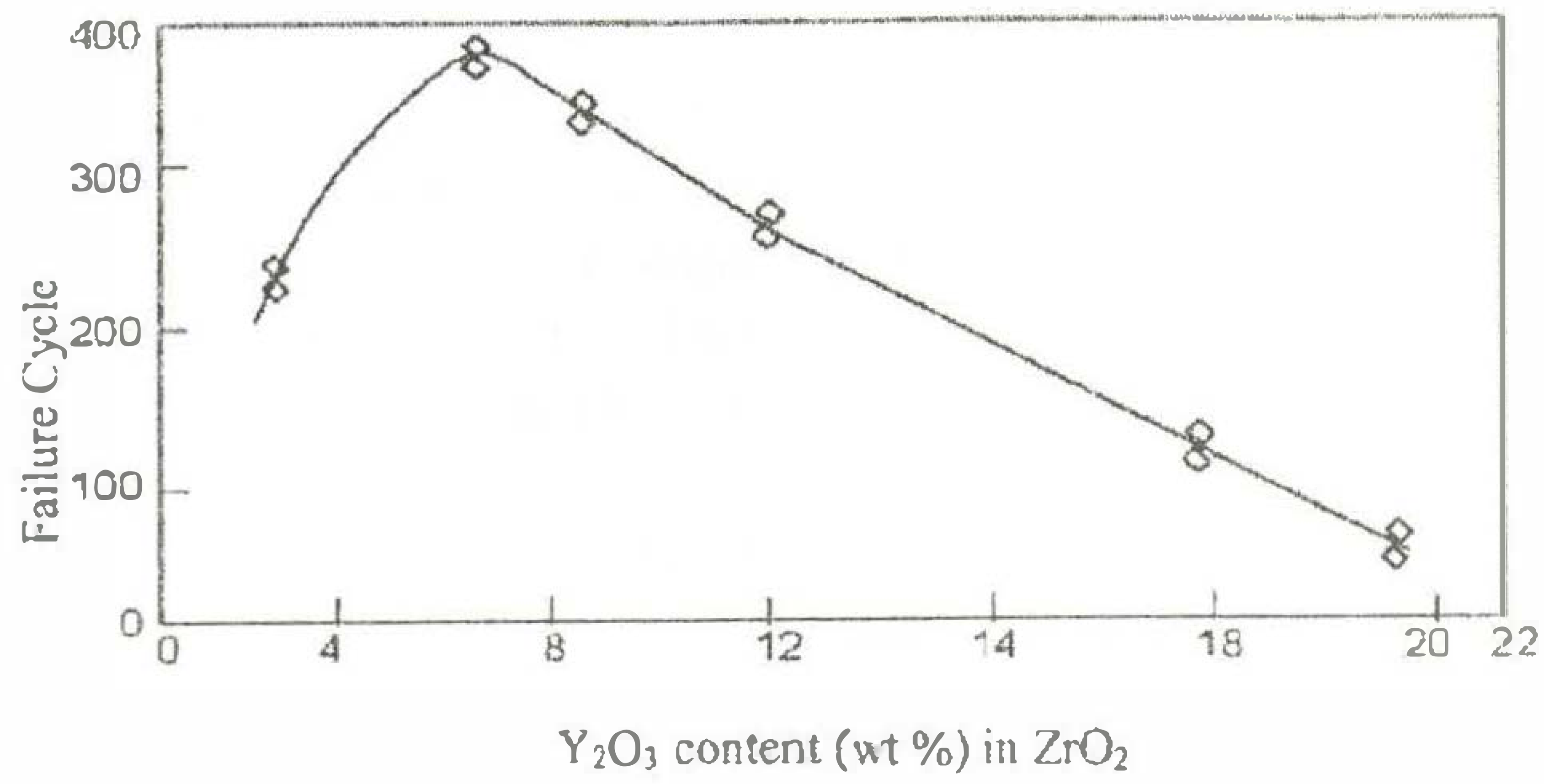

Figure 1. The effect of Y_2O_3 Content (wt %) in ZrO_2 on TBC life (16).

III. IMPROVEMENTS IN THE PROPERTIES OF TBC

It is possible to increase the mechanical and thermal shock strength of the ceramic coating materials by means of the stresses within the compounds with two phases which consist of monoclinic and tetragonal zirconia. Zirconia with two not fully stabilised phases is called partially stabilised zirconia (PSZ). The strength of Y_2O_3-PSZ has been substantially increased when the amount of Y_2O_3 reduced from 6 % mole to 3 to 4 % mole. The volume of zirconia increases approximately 5 % when cooled below transformation temperature. This is due to structural transformation of zirconia from tetragonal to monoclinic phase. Tangential stresses at the grain boundaries of PSZ cause formation of micro cracks. These micro cracks within the structure create damping effect against crack propagation and hence improving toughness property of the PSZ [15].

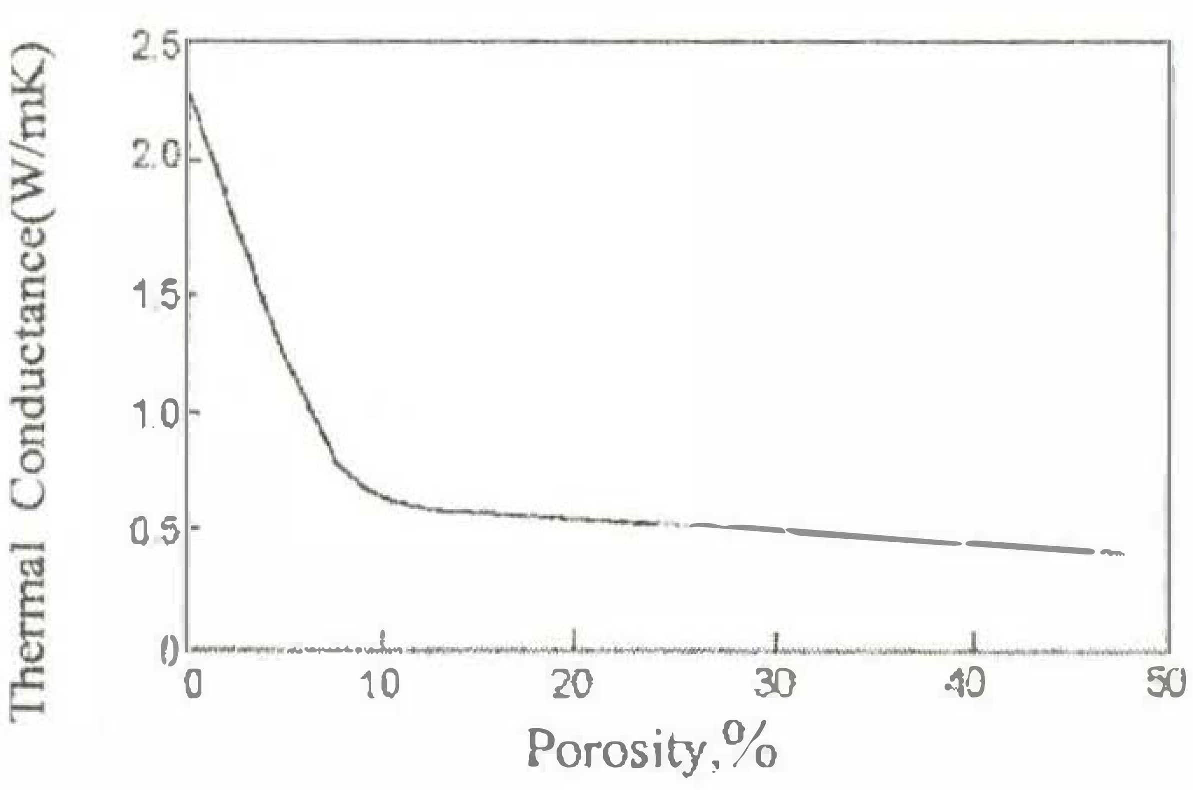

Figure 2. Variation of thermal conductance of Y_2O_3- ZrO_2 depending porosity, % (16).

TBC developed for aircraft engines to achieve both component temperature reduction and oxidation resistance is a two-layer coating. These layers consist of metallic inner layer and an outer insulating ceramic layer. The ceramic layer typically is plasma sprayed ZrO2 partially stabilised with 6 to 8 wt % Y2O3. Figure 1 shows the effect of Y2O3 portion (wt %) in ZrO2 on TBC failure [16].

It is imperative to reduce the amount porosity within PSZ in order to improve corrosion resistance. In addition coating materials are required to be chemically inert to the exposed environment. However, the amount of porosity is kept at a certain limit due to the necessity of low thermal conductivity for TBC applications. Figure 2 shows the effect of porosity variation (%) on thermal conductivity.

The life of coating is related to its density. As shown in Figure 3, the life of coating reaches a maximum with increasing density to a certain limit. However, beyond a certain level, increasing density lowers the coating life.

The thickness of the inner metallic bond coat (MCrAlY, M≡ Ni or Ni+Co) is approximately 0.13 mm. Bond coat protects the substrate against oxidation as well as providing a relatively rough surface for better adherence of the top ceramic coat. The bond coat is required because the ceramic top coat is not capable of providing any oxidation resistance to the substrate.)

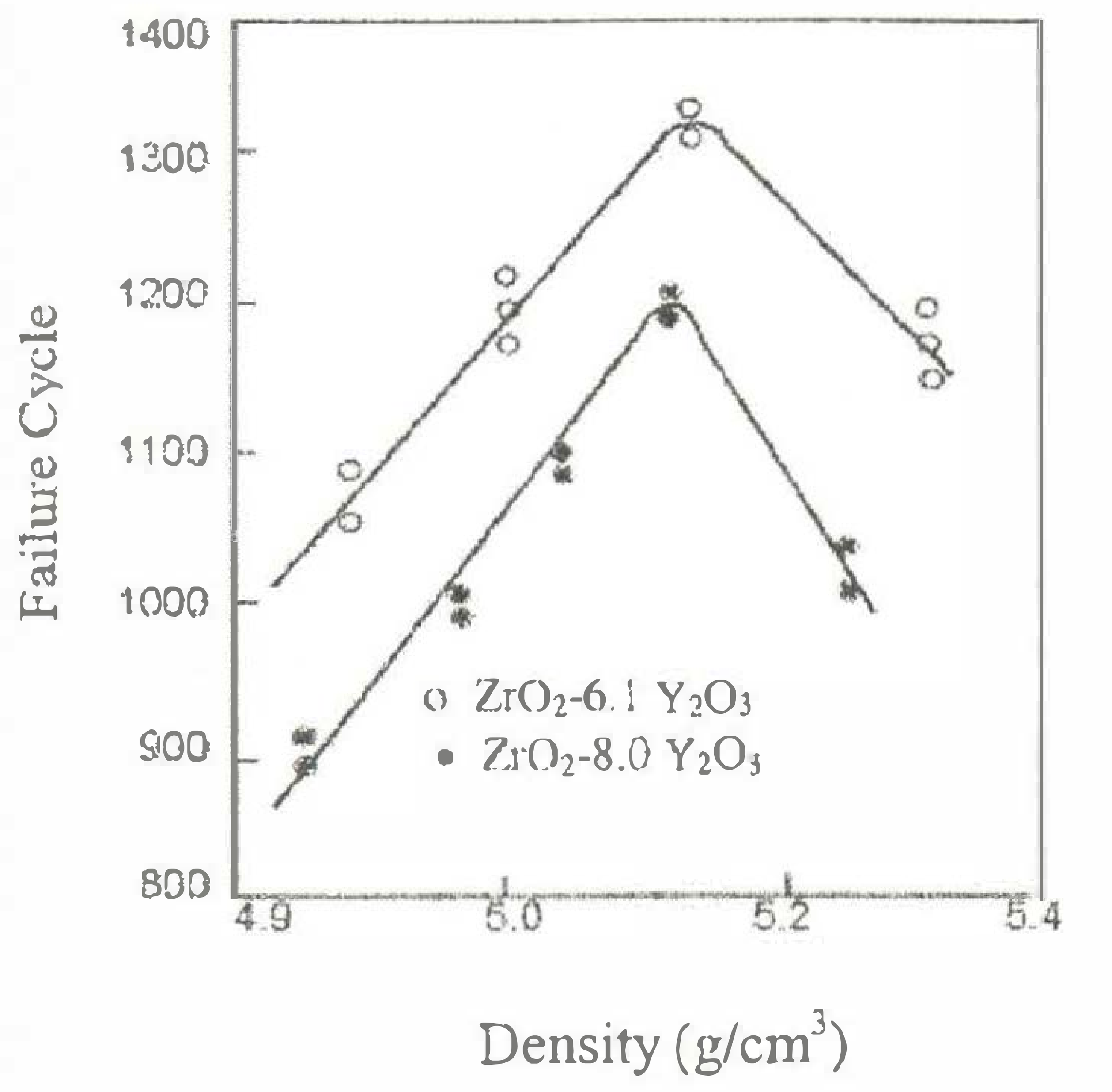

Figure 3. The effect of density of Y_2O_3-ZrO_2 on TBC life (16).

Oxygen can easily diffuse to metallic bond coat owing to the high porosity, segmentation and ionic conductivity of the zirconia top coat. The bond coat suffers oxidation attack. An oxide layer builds up between bond coat and top coat and the related volume expansion causes internal stress at this interface. When the oxide layer has attained a critical thickness, cracks can first be observed. With increasing oxidation attack the ceramic spalls off. Bond coat oxidation also influences the thermal shock resistance with increasing oxidation attack the number of thermal shock cycles to failure is reduced. As a consequence of the oxidation-based failure mechanism, bond coats with higher oxidation resistance were developed. The most important development were

- Optimisation of the chemical bond coat composition from NiCr to NiCrAl to the MCrAlY alloys (M ≡ Co or Ni),
- Improvement in the application of techniques:Low pressure plasma spraying, which increases the oxidation resistance at the same chemical bond coat composition.

As for the chemical composition, the oxidation resistance of bond coats seems to be optimised. Further improvement in the oxidation resistance will be possible by the use of oxygen diffusion barriers. Thomas at al. suggested a new oxidation-resistant thermal barrier coating that consists of a three-layer system[21]. This system is as follows:

- On to a substrate an MCrAlY bond coat applied by low pressure plasma spraying,
- An Al_2O_3 diffusion barrier produced by reactive sputtering, the diffusion thickness varies from 2 to 5 μm ,
- On to the diffusion barrier a 200 μm ZrO_2-8%Y_2O_3 top coat sprayed by plasma under atmospheric conditions.

Oxidation resistance is influenced Al content in the bond coat composition. Increasing percent of the Al content in composition makes the coating brittle. To enhance this difficulties, Re is added into CoNiCrAl bond coat. Re also improve the mechanical properties of the coating material [22].

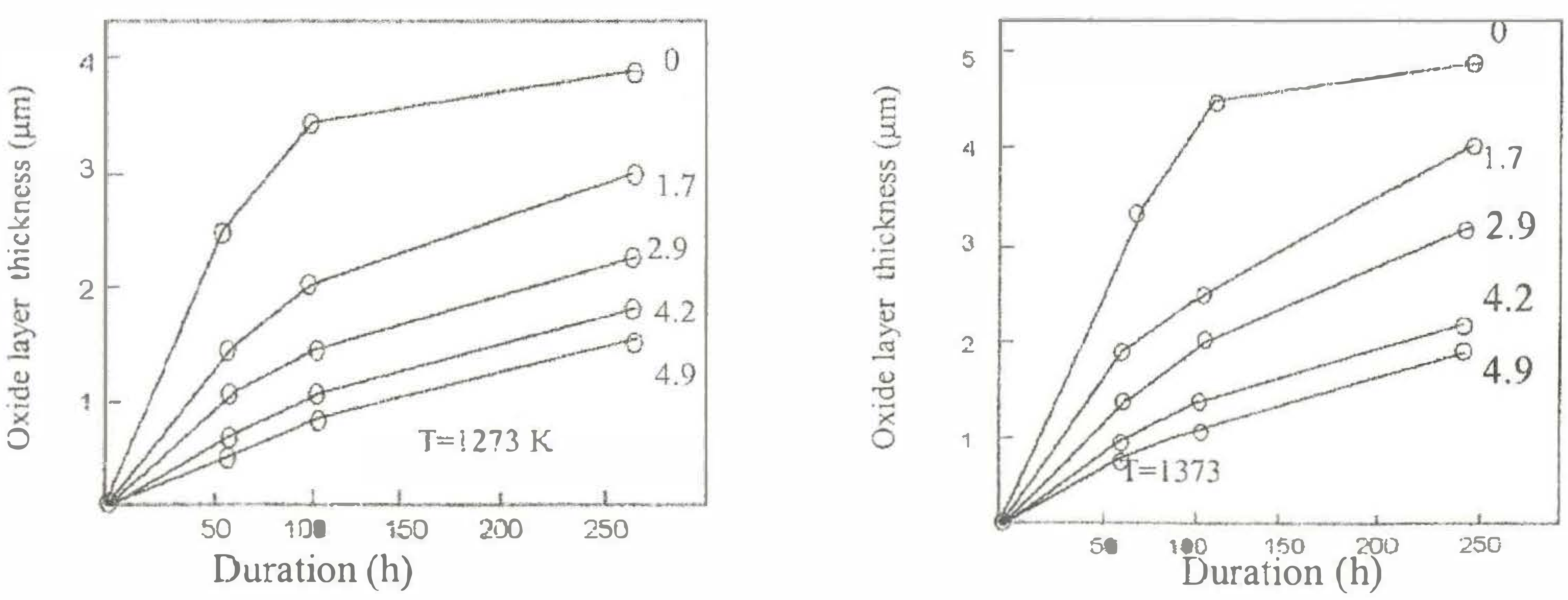

Figure 4. Variations of oxide layer thicness with respect to diffusion barrier coating thicness at 1273 K and 1373 K. The bond coat composition is Co-31Ni-21Cr-8Al-0.5Y(21)

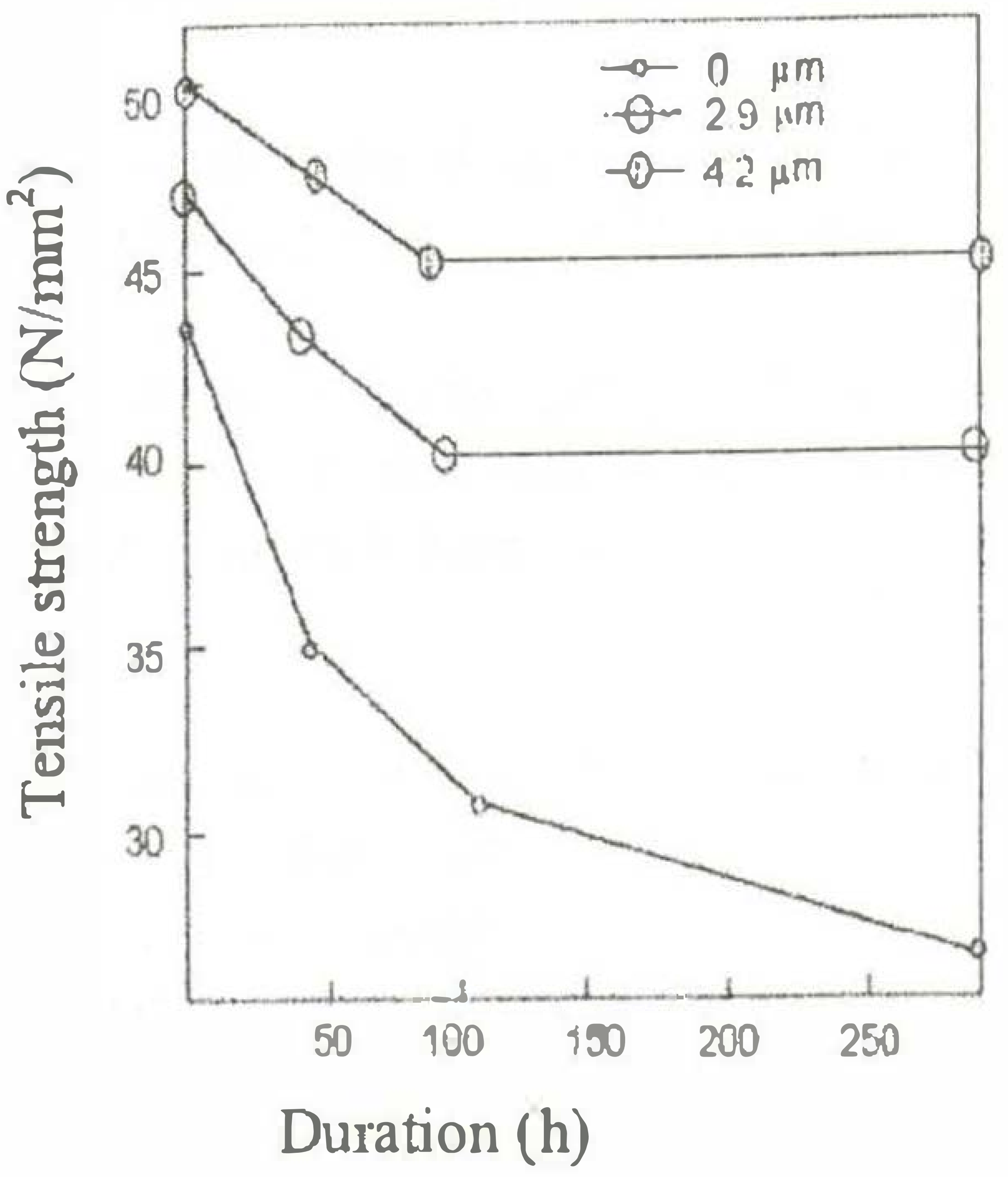

Figure 5. Tensile strength variation at the interface between top coat and bond coat after 10 thermal shock cycles [21]

Tolukan et al. [23] reported that the application of fiber-metal bond coat reduced the stresses associated with thermal property mismatches, showed outstanding performance when subjected to severe thermal shock tests. They proposed that this application contributed substantially to the betterment of thermal and oxidation resistance of the ceramic coating.

IV. CONCLUSION

Application of multiple-layer coating in internal combustion engines to prevent thermal property mismatch and reduce oxidation yields promising results. When applied on a bond coat of MCrAlY, Al2O3 layer of 2-5 microns, which serves as a diffusion barrier, reduced oxidation to an important extent.

For the TBC to be of long service life, porosity, ratio of stabilizer and density of TCB were highlighted to be the important parameters. However these parameters need to be optimised depending on the type of ceramic coating material and working conditions. According to the relevant sources, 6-8 % mol Y2O3-PSZ and theoretical TBC density of 90% produce the best results.

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