To study the effect of Tazheranite phase on hardness, applied Calcia Stabilized Zirconia on Al6061 and Gray Cast Iron

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Abstract: Tazheranite is the modified form of cubic zirconia.It plays a significant role, to alter the micro hardness of surface of the applied coating ($Al_2O_3+ZrO_2.5CaO$).Present experimental work is to investigate the effect of Tazheranite (rare mineral) phase on micro hardness of the top coat applied pure ceramic on Al6061 and Gray Cast Iron substrates. Tarzheranite phase perceived in Xrd analysis during Air plasma coating in this experimental work.

Keywords: Tarzheranite, Local particle density, Thickness, Porosity, Microhardness.

I. INTRODUCTION

Thermal barrier coating here after called (TBC) is used to protect the operational members from large and prolonged heat loads to realize high degree of functional and economical excellence from the graded coated systems. Principally functionally graded coating consists of more than two layers viz. number of bond coats followed by unique top coat. Each distinguishing deposit serves as a means for shielding the components from aggressive environment.

A lot of literatures are available on Yettria stabilized Zirconia subsequently called (YSZ), finds application in rugged environment used as TBC [1]. YSZ is the first preference among the researchers since last two decades because it possesses specific mechanical and thermal properties. In the present study specific percentage of Calcia Stabilized Zirconia henceforth called (CAZ) added in Alumina, replacing YSZ, to achieve unique mechanical and thermal properties, applied as a functionally graded coating on Al6061 and GCI.

To determine the life span of TBC hardness is one of the important parameters which get affected by various process parameters [2].Micro hardness of the top coat of pure ceramic significantly altered by specific weight percentage of Calcia Stabilized Zirconia (CAZ) present in Alumina.

CAZ are gaining more attention compared to YSZ due to formation of Tarzheranite, transformed cubic crystal structure of Calcia stabilized zirconia in alumina, during solid-state reaction, which cause asymmetric change in microhardness.

Very limited papers and less exploration has been done on Tarzheranite phase. Hidehiko et.al. described the presence of Tarzheranite phase and addressed abut its thermal conductivity in special composition of calcia stabilized Zirconia [3]

Porosity is microstructure feature. Porosity, results of thermal mismatch [4] of constituent material during phase transformation, is a key parameter to determine microhardness. Thickness of the coating is other affecting parameter of porosity by altering local particle density of coating.

Image analysis shows local particle density is a function of thickness, which increases as thickness increases. Porosity, determining factor of microhardness, caused due to thermal mismatch among different constituent in graded system and substrate also Porosity caused by Thermal mismatch among different constituent in graded system and substrate play important role to measure micro hardness.

Porosity is also commonly needed in ceramic thermal barrier coatings (TBC), extensively used in aircraft and land-based turbines and diesel engines. Porosity also increases thermal shock andthermalcycling(fatigue)resistance [5].In this paper an exertion has been made to explore the potential of newly developed phase formed due to solid state reaction and at the same time investigate the variation of micro hardness due to various reasons viz. thickness, particle size, porosity etc.

II. EXPERIMENTAL PROCEDURE

2.1 Atmospheric PlasmaSpraying
The substrates Al6061 and GCI used for the present study and were coated by Air plasma technique. The feed stock was in the form of powder provided by Sulzer Metco.

The coating was developed on 100×100×5 mm Al6061 and GCI samples. Before the substrates subjected to preliminary investigations 10×10×5 mm substrate sliced from the above specified dimensions.

To achieve high coating hardness and also good deposition efficiency a small argon flow rate, a high current as well as small spraying distance monitored (Ref.2). The spray parameters are adopted (Refer table 1)

Sr. No.	Specifications	Parameters
1	Plasma gun	3 Nylon Brush
2	Nozzle Temperature	10,000 ^{0}C
3	Current	500 Amps
4	Voltage	65-70 Volts
5	Powder feed	45-45gm/min
6	Spray distance	50.8-78 mm
7	Primery gas(Argon)	3.7 Bar
8	Secondary gas, Hydrogen	3.45 Bar

Table 1: Air Plasma machine Specification

2.2 Determination of coating thickness

To begin with the total thickness of the top coat i.e. ($ZrO_2.5CaO+Al_2O_3$) was intended to be applied 100,200 and 300 µm - over Al6061 and GCI substrates. Initially three stage of polishing were done using aluminium slurry abrasive, paper of reducing grit size (46-58) µm and then diamond paste on the wheel & were fixed on the acrylic material show in figure 1.

Fig.1

The thickness of the coating was measured using optical microscope, model: Clemex CMT.HD in the present investigation coating thickness values were express in microns & error percentage in coating thickness calculated for the top coat samples using empirical relations given below.

$$\frac{Tth - Tact}{Tact} \times 100 \quad (Eq\ 1)$$

2.3 Determination of Hardness and Porosity

As per ASTM E- 384 standard (Ref.1) the micro hardness of the test samples (Al6061 and GCI) were determined using Clemex Vicker micro hardness tester under following parameters (Refer table 2) The microhardness measurement was carried out on the transverse section of top coat, middle coat and bond coat.

An average of three readings was taken at different locations interphase of the coating system, mid-section area on all the coating system in order to achieve greater accuracy. Increased particle velocity, higher amount of unmolten particles leads to more voids within the coating. There may be some kind of bouncing–off effect leads to higher porosity, affecting hardness.

Porosity analysis was carried out by means of microscope equipped with a CCD camera model: cmt.hd the digitized image captured from the polished surface at the cross section. The image is taken & converted into a rectangular array of integers and the analysis software automatically measures the fraction of pores from the selected area.

Sr.No.	Specifications	Parameters
1	Load	100 kgf.
2	Dwell time	10 sec.
3	Indenter	Diamond pyramid (120^0)

Table 2: Vickers micro hardness test operating conditions

2.4 X-Ray Diffractometer and particle size

Xrd analysis was based on search match program that is used to compare experimental diffract gram with pattern of known compounds included in data base of joint committee powder diffraction standard (JCPDS). Phase transformation, crystal structure, weight percentage of different phases, particle size was determined using XRD technique. (Particle size was determined using scherrer equation and full width half maximum (FWHM) graph. XRD machine specifications refer table 3 and operating parameters were considered during the analysis. Powder Diffractometer (PW1880, Philips, Almelo), operating with CuKα1 radiation produced at 40 kV and 40mA.The θ-2θ scan was performed between 20 and 89.99^0 by step width of 0.01036^0.

Sr.No.	XRD Machine Specification	
1	Make	Brukar
2	Model	D8 Advance
3	Measuring circle diameter	435,500,600
4	Smallest addressable increment	0.0001^0
5	Reproducibility	0.0001^0
6	Anode	Cu, Cr, Co
7	Detector	Scintillation & Lynxeye

Table 3: XRD machine specification

III.   RESULT AND DISCUSSION

In the present work two coating systems are developed comprises of Al6061 and GCI. On Al6061 substrate two bond layers applied in which one is metallic powder (Metco-446)Al25Fe7Cr5Ni followed by cermet (Metco410NS) Al2O330(Ni20Al).

Coefficient of thermal expansion (CTE) is less compared to Al6061 therefore only one bond coat (Metco-452) Fe38Ni10Al is applied to mitigate the thermal mismatch among functionally graded layers.The top coat for both the system is pure ceramic, consist of mixture of Alumina (Metco-105SFP) Al2O3 and Calcia stabilized zirconia (Metco-210NS) ZrO2.5CaO in 50:50 proportion were applied. The top coat thickness for both the substrate varied as 100,200,300 µm. The samples are subjected to

microstructure study, measurement of coating thickness using scanning electronic microscope followed by XRD, Porosity, and Micro hardness.

3.1 Coating Thickness measurement

SEM technique was adopted to determine the actual thickness of the applied thermal barrier coatings and also percentage error calculated shown in graph 1.The error of 39.3% found in case of 100µm top coating of Al6061 & GCI. Moderately less error encountered in case of 200 and 300 µm top coating system. The error percentage of the top coat can be reduced by adopting automatic or robotic plasma coating technique.
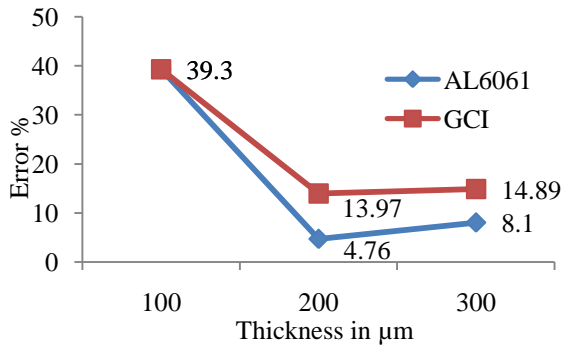
Graph 1: Top coat error percentage vs. thickness
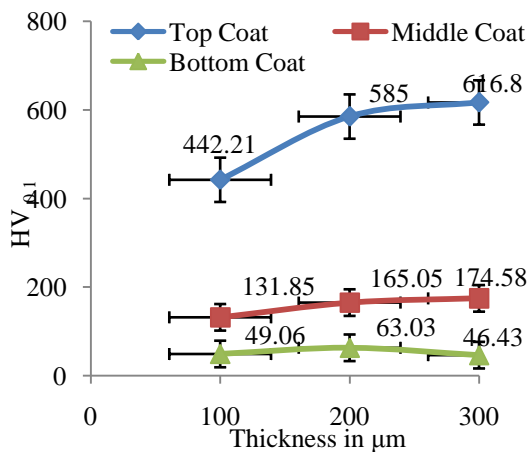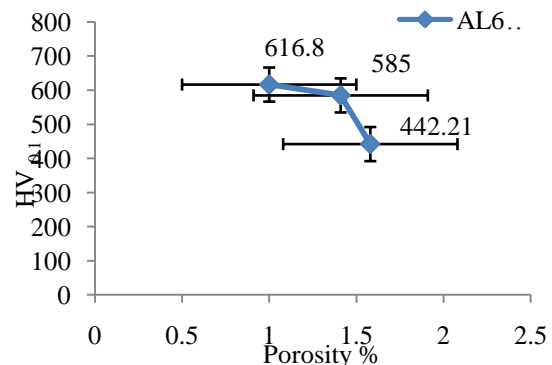

Graph 2: Hardness vs. Thickness(Al6061)
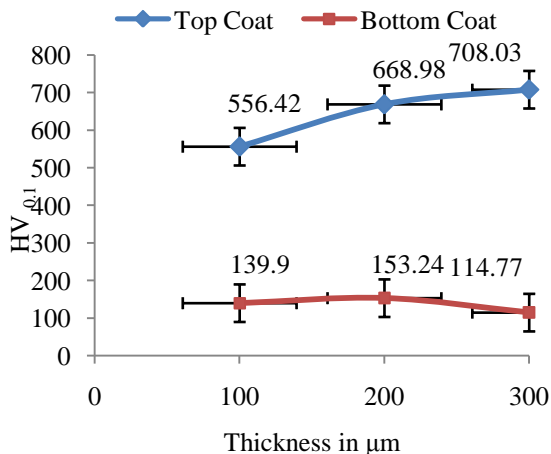
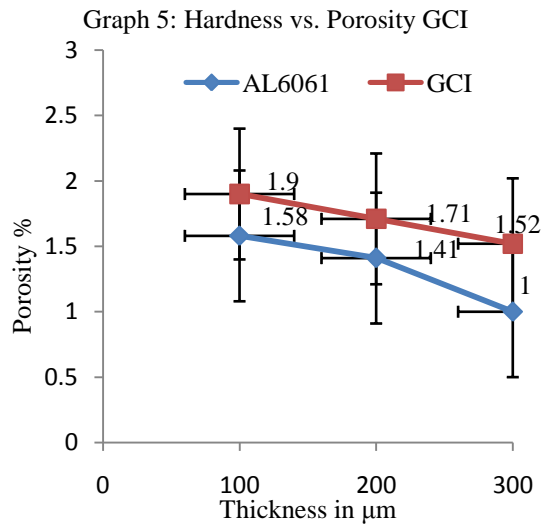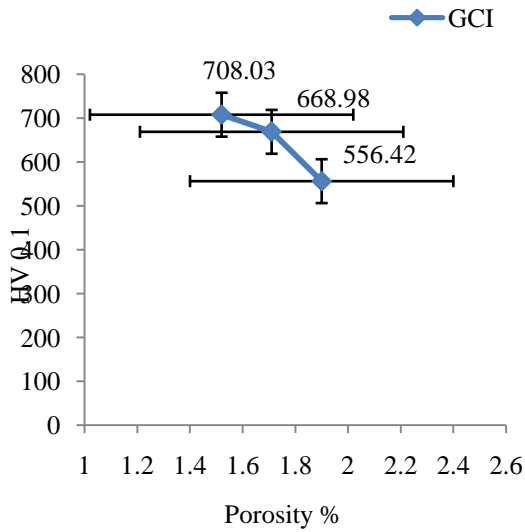Graph 3: Hardness vs. Thickness (GCI)

3.2 Hardness versus Thickness

A repeated work of coating by varying its top coat thickness revieled that the thickness is the influencing parameters affecting the hardness of the top coat.The weight percentage of Tarzhenite phase leads to increase hardness with increase in thickness refer graph 2 and 3 also formation of tiny particles results in slightly higher hardness than the 100 µm& 300 µm coating thickness for metallic powder coatings.But in case of cermet and ceramic as thickness increases hardness also increases.A noticible increment percieved in case of pure ceramic hardness increases with increase thichness with increase weight percentage of Tarzhenite phase.Similar result revealed in case of GCI where hardness is slightly less at 300 µm compare to 100 µm and 200 µm because a good adhesion exhibit between substrate and cermet(Metco-452) Fe38Ni10Al preventing to form tiny particles,as thickness causes slightly decrease in hardness.But in case of pure ceramic hardness increases with respect to thickness.A very good adhesion reported to be existing in between cermet & pure ceramic with the specific composition which significantaly enhance the hardness of the top coat.

3.3 Hardness versus porosity

From graph 4 and 5 it is evident that decrease in local particle density leads to increase in porosity of the top coat resulting decrease in hardness of the top coat found in both the case of Al6061 and GCI.

Graph 4:Hardness vs. Porosity AL6061

Graph 5: Hardness vs. Porosity GCI

Graph 6: Porosity vs. Thickness

3.4 Porosity versus thickness

Porosity and thickness is the main characteristics of any TBC system which affects the various properties of the coating system like microhardness,wear and tear,thermal sustanability etc. but porosity is the function of thickness which is altered by various process parameters and local particle density during solid state reaction.Graph 6 shows porosity decrease with increase in thickness.

3.5 X-Ray Diffraction Investigations

Tazheranite as major phase perceived during XRD analysis whose weight percentage is more compared to Aluminium Zirconium oxide phase in the admixture of (Al_2O_3 ZrO2.5CaO) refer graph 7(a) & 7(b). As per mineral data report this mineral exhibit high thermal expansion(α=11*10-6 K), excellent thermal insulation,low thermal conductivity (2.5-3w/mk)very high resistance to crack propagation,high fracture toughness (6.5-8 MPa),high melting point and high resistance to acid [6]also Scherer equation refer equation 2 and FWHM fig.7 (c) were used to calculate particle size. The average particle size is found to be around 411Å.

$$\tau = \frac{K\lambda}{\beta \cos\theta} \text{ (Eq 2)}$$

- τ is the mean size of the ordered (crystalline) domains, K = 0.9 is a dimensionless shape factor, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM), θ is the Bragg angle.

Sr. No.	Parameters	Values
1	λ	1.55060 Å
2	FWHM (β)	$3.4906*10^{-6}$ radian
3	K (spherical)	0.9
4	θ	0.9652 radian

Table 4: XRD operating parameters

It is also evident from the XRD results, the shape of the crystals are cubic even after change in phase (Tazheranite) at the same time little amorphous matter realized shown as graph 7(a) and 7(b) small peaks. Since most of the crystals are of the same family, very good stacking of crystals predicted.
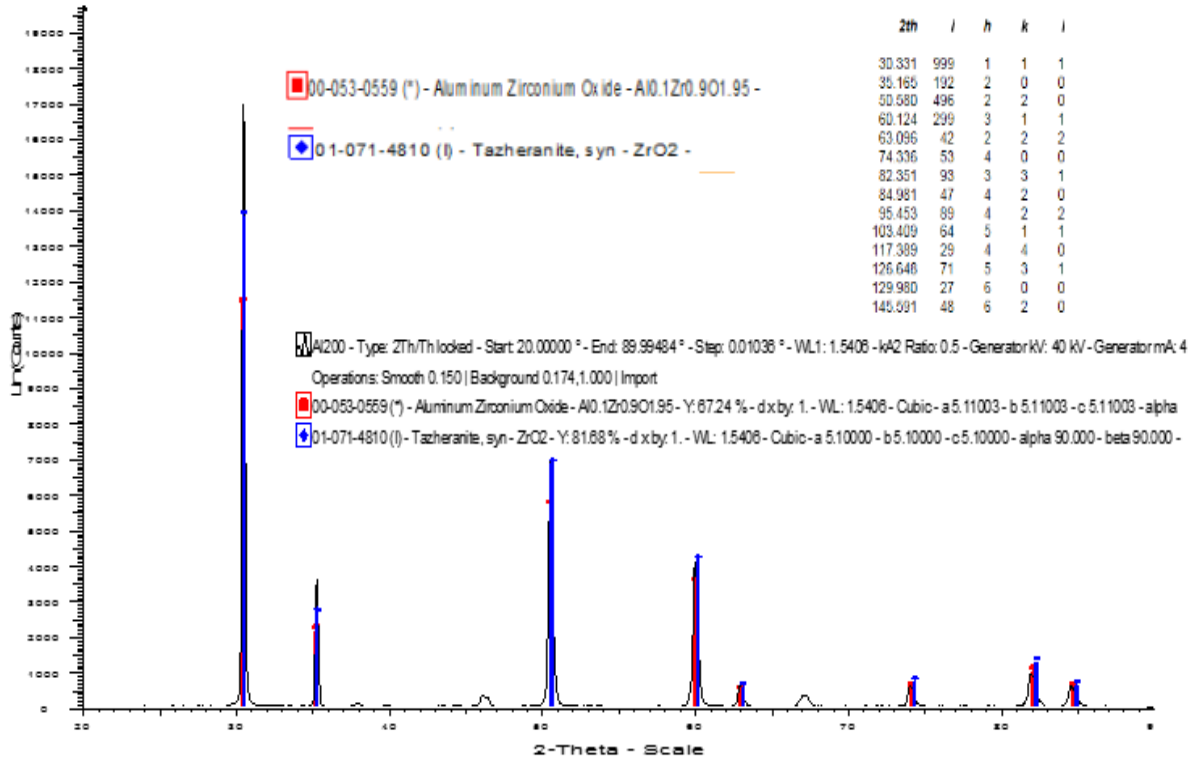
Graph-7(a) XRD pattern of (Al$_2$O$_3$ ZrO$_2$.5CaO) topCoatapplied on Al6061
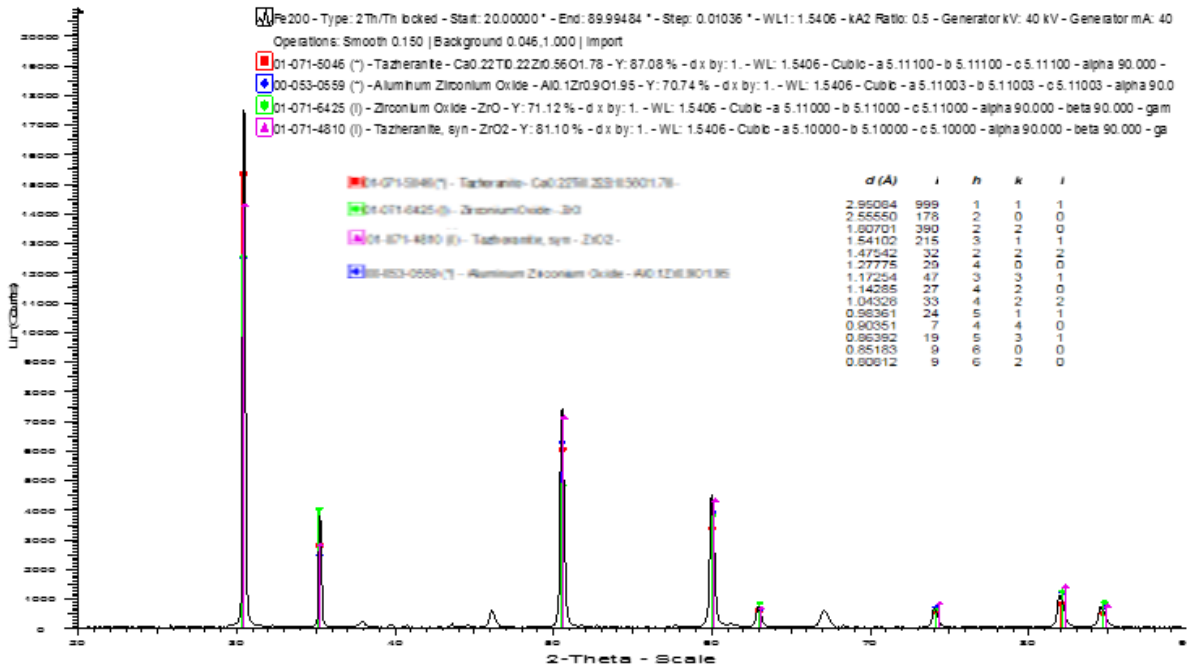
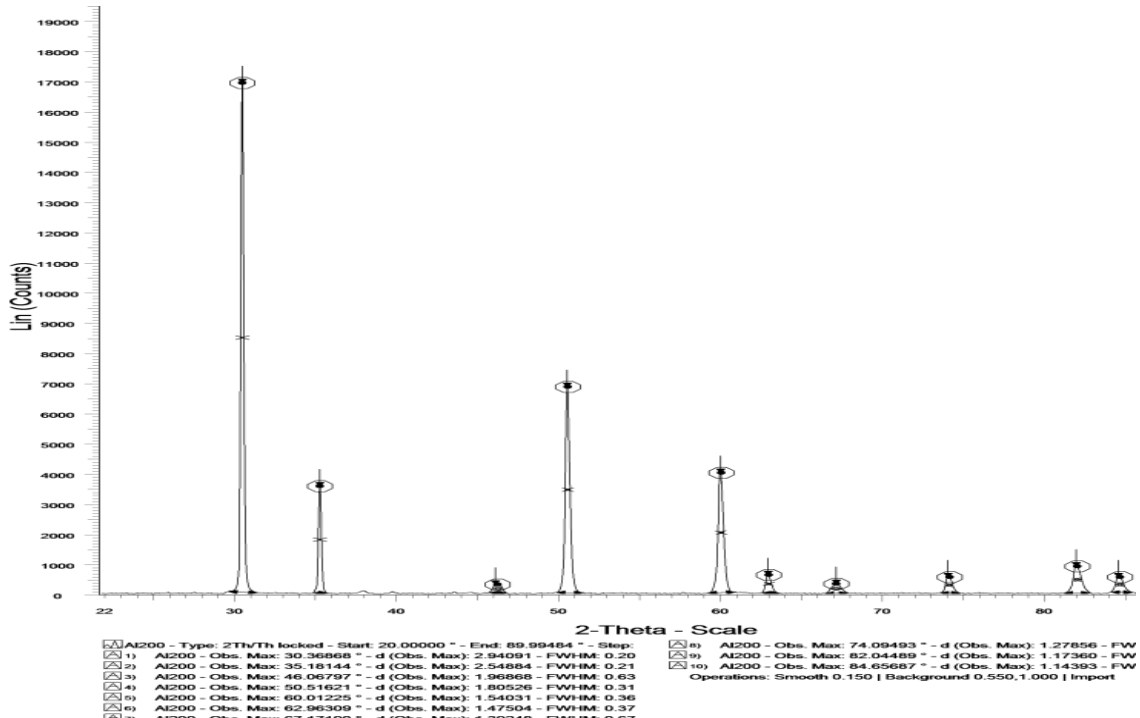Graph-7(b) XRD pattern of (Al$_2$O$_3$ ZrO$_2$.5CaO) topCoat applied on GCI

Fig- 7 (c) Full width half maximum (FWHM) pattern of (Al_2O_3 $ZrO_2.5CaO$) top Coat applied on Al6061

IV. CONCLUSION

A new type of coating system were developed, fifty percent of alumina blended with fifty percent of calcia stablized zirconia $ZrO_2.5CaO$ as a top coat, $Al_2O_3$30 (Ni20Al), Al25Fe7Cr5Ni as bond coats on Al6061 and Fe38Ni10Al bond coat over Gray cast iron substrate by means of Air Plasma Technique.

1) Hardness is the strong function of porosity, when porosity reaches more than 1% a rapid decrement in hardness percieved.
2) As the thickness increases the hardness of the top coat significantly increases compared to middle coat and bottom coat.
3) For bottom coat hardness decreases unlikely Al6061 as thickness increases but for top coat hardness increases with respect to thickness.
4) As the coating thickness increases porosity decreases for Al6061 and GCI.
5) Formation of Tazheranite phase for the Alumina (Al_2O_3) and Calcia stabilized zirconia ($ZrO_2.5CaO$) in 50:50 proportions alter the top coat hardness whose average value found 708.3HV0.1 & 616.8HV0.1 on GCI & Al6061 respectively.

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