Eng. & Tech. Journal, Vol.27, No.16, 2009

Study Some of the Structure Properties of ZrO_2 Ceramic Coats Prepared by Spray Pyrolysis Method

Dr.Ali H.Ataiwi *& Dr.Alaa A. Abdul-Hamead*

Received on:15/3/2009
Accepted on:1/10/2009

Abstract

In the present work pure and doped ZrO_2 with (Al and Co 5wt%) thin film has been deposited on glass and stainless steel 304 substrates by spray pyrolysis technique The film were tested by XRD and the topography of the films has been examined by using SEM. Open porosity, rate of deposition, surface roughness and apparent density was calculated . The results of XRD show that the films was crystalline with tetragonal phase of ZrO_2 .The grain size of pure ZrO_2 was (148.6 nm) and lattice strains was 0.27%.Apparent density for pure ZrO_2 and with(Al,Co) dopents were (4.5,5 and 5.5 g/cm^3) respectively ,and open porosity for the films are respectively(2.5,2 and 1.5 pore/cm^2). Surface roughness (Ra) was(0.218µ m) for pure ZrO_2 film and(0.904µm) for ZrO_2 doped with Al.

دراسة بعض الخواص التركيبية لطلاءات الزركونيا ZrO_2 السيراميكية المحضرة بطريقة الرش الكيمياوي الحراري

الخلاصة

في هذا البحث تم ترسيب طلاء من الزركونياZrO_2 النقية و الزركونيا المشابة بنـــوعين مـــن المعادن وهي الالمنيوم و الكوبلت بطريقة الرش الكيميائي الحراري وبنسب وزنيه بلغت(5 wt%)لكل منهما على قواعد من الزجاج والفولاذ304.تم اولا تحليل الاغشية بأستخدام حيـــود الأشـــعة الســـينية XRD و فحص البنية المجهرية باستخدام المجهر ا لالكتروني الماسح وكذلك تـــم قيـــاس المســـامية المفتوحة و حساب الكثافة الظاهرية و معدل الترسيب,و الخشـــونة أيضـــا . بينـــت نتـــائج XRD ان الاغشية المترسبة كانت متبلورة والطور المتكون هو(مربع الزوايا و الإضلاع) و الحجـــم الحبيبـــي للزركونيا النقية بلغ(148.6 nm) ونسبة الاجهادات الداخلية(0.27%).بلغت قيمة الكثافة الظاهريـــة لاغشية الزركونيا النقية (4.5g/cm^3)و للأغشية المشابه بالالمنيوم و الكوبلت هـــي (5.5g/cm^3 ,5) على الترتيب, قيمة المسامية للزركونيا النقية بلغت (2.5 Pore/cm^2) و للمشابة بالالمنيوم و الكوبلـــت (1.5,2 Pore/cm^2) على التوالي .بلغت قيمة الخشونة السطحية لاغشية الزركونيا النقية (Ra=0.218µ m) و المشابة بالألمنيوم (0.904µm).

Introduction

Ceramic coatings can improve the chemical and mechanical durability of steel at higher temperature [1]. To gain this improvement coatings can be applied.Spray pyrolysis coating is a technology used to improve surface properties of a wide range of substrate materials, including glasses, ceramics, plastics and metals, [2, 3]. However, the development of spray pyrolysis

• Materials Engineering Department, University of Technology /Baghdad

https://doi.org/10.30684/etj.27.16.4
2412-0758/University of Technology-Iraq, Baghdad, Iraq

coatings on substrate is challenging, because ceramics are considered to be heterogeneous systems, which possess more complex compositions than other materials. Thin oxide film have found application in many areas ranging like precision ball valve balls and seats**,** high density ball and pebble mill grinding media, oxygen sensors**,** fuel cell membranes**,** electric furnace heaters over 2000°C in oxidizing atmospheres**,** cutting tool and engineering application like high level waste packaging, microelectronic application [4,5,6,7].D.NGUYENM prepared $ZrO_2$and $Al_2O_3.ZrO_2$ films by spray pyrolysis by using $Zr(C_4H_9O)_4$ and studied the film by using XRD and SEM. He found that the structure of these films is amorphous and structure after annealing at (550Cº) became crystalline structure. Zircona is one of the most import thin oxide film materials because of their favorable dielectric properties, low thermal conductance and high wear and corrosion resistances[8].Oxide wear resistant coatings used in industrial application can be prepared by many techniques .JOHN D. (2008) made a review on the methods used to prepare ceramic films like TiN , Al_2O_3 and ZrO_2[9].Spray pyrolysis is attractive because it is a low cost technique[2], therefore ZrO_2 coating was prepared by spray pyrolysis though it is relatively rare[10].The aim of this work was to prepare ZrO_2 coating by spray pyrolysis method and study some of the structure and texture properties of ZrO_2 ceramic coats prepared.

Experimental section

In this work an aqueous solution of zirconium chloride ($ZrCl_2$) has been used to prepare ZrO_2films. The concentrations was (0.1 Mole). The acidity was maintained to be 4-5 pH during spraying .Two salts [$AlCl_3.6H_2O$, and $CoCl_2.6H_2O$) were used to dopent ZrO_2 film with elements (Al and Co) at (5wt. %) for each dopant respectively. The deposition of the films is made by spray pyrolysis technique. The spraying apparatus was manufactured locally in the university laboratories. In this technique, the prepared aqueous solutions were atomized by a special nozzle glass sprayer at heated glass with dimension $(2*1.5*0.2)cm^3$ and stainless steel 304 with dimension $(1*1*0.5\ cm^3)$ substrates fixed on thermostatic controlled hot plate heater. The chemical composition of the stainless steel was tested by using Portable-Met. analyser as listed in table (1). Air was used as a carrier gas to atomize the spray with the help of an air blower. The substrate temperature was maintained at 400 °C during spraying with (±10 ^oC). To avoid excessive cooling of the substrate, spraying was achieved in periods of about (5 second) followed by (2 min) wait. Deposition rate was about(4 nm/s) with (2.5 ml/min) of flow rate. To deposit films of uniform thickness the distance between the substrate and spray nozzle was kept at (15±1 cm.) The spray of the aqueous solution yields the following chemical reaction [11]:

$ZrCl_2 + 2H_2O \xrightarrow{400C^\circ} ZrO_2 \downarrow + Cl_2 \uparrow + 2H_2\uparrow$ ……… (1)

Each one of the doping elements is precipitated according to the reaction below:

$2AlCl_3.6H_2O \xrightarrow{400C^\circ} 2\,Al \downarrow + 3\,Cl_2 \uparrow + 12H_2O\uparrow$ ……… (2)

$CoCl_2.6H_2O \xrightarrow{400C^\circ} Co \downarrow + Cl_2\uparrow + 6H_2O\uparrow$ ……. (3)

ZrO_2 thickness t was calculated from the relation below, and it was 2µm[12]:

$$t = \frac{\Delta m}{r' \times A} \quad ……………..(4)$$

Where Δm is the mass changes of the substrate before and after deposition ,ρ' is theoretical density of ZrO_2 coat and A is substrate area .

The properties of X-ray diffraction was used from diffractometer type CuKα with(λ = 1.54056 Å), the scanning speed was 3%. The data was compared with that ASTM (14-0534) card .To determine the (a- and c-lattice constant) from X-ray spectrum were using the following formulas [13]:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \quad ……..(5)$$

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2} \quad ……… (6)$$

Where (hkl) are Miller indices, d-space (inter planer space) which can be calculated from the well-known BRAGG's law [13]:

$$n\lambda = 2d_{(hkl)} \sin\theta \quad ….. (7)$$

The preferred plane (hkl) in polycrystalline coat in which there is maximal growth (preferred orientation) can be described by texture coefficient [14]:

$$Tc(hkl)=[I_m(hkl)/I_{ASTM}(hkl)]/[(1/M)\sum I_m(hkl)/I_{ASTM}(hkl)] \quad ………………(8)$$

Where $T_C(hkl)$ is the texture coefficient of the (hkl) plane, I_m is the measured intensity, I_{ASTM} is the **A**merican **S**tandard for **T**esting **M**aterials ASTM standard intensity of the corresponding powder and M is the number of reflections observed in the X-ray diffraction trace.

The average grain size (g.s) of the crystalline material which plays an important role in the material properties can be estimated easily from the X-ray spectrum by **F**ull **W**idth of **H**alf **M**aximum (FWHM) method that is often represented by[15]:

$$g.s = \frac{K'\,l}{B\cos q} \quad …… (9)$$

Where K' is constant and about 1, B is the width of the half maximum of the peak (111).

The strains (δ) arising from the microstresses or microtensions in the lattice cause a deviation in the c-lattice constant of the tetragonal structure from the standard ASTM value. This deviation can be evaluated from the following relation [15]:

$$d = \frac{|c_{ASTM} - c_{XRD}|}{c_{ASTM}} \times 100\% \quad ……(10)$$

Where c_{ASTM} is the c-lattice constant according to the ASTM card and c_{XRD} is that measured from XRD spectrum. Lattice mismatch between substrate (stainless steel 304)and upper coat layer ZrO_2 can be evaluated from the following relation[16]:

$$\text{Lattice Mismatch} = \frac{2|a_2 - a_1|}{a_2 + a_1} \times 100\% \quad ..(11)$$

Where a_2 is lattice constant for ZrO_2 coat and a_1 is lattice constant for substrate (stainless steel 304).

The topography of the ZrO_2surface was inspected with SEM.

Surface roughness (Ra) was achieved by using roughness tester type TR 200 .Apparent density (A.D) was calculated from relation:

$$A.D=\Delta m/t*A \quad .... (12)$$

Where t is coat thickness.

Open pores was measured by used prop point method ASTM (D3258-04)[18].

Results And Discussion

Figure (1) shows XRD chart of pure ZrO_2 film from which was observed that the film was polycrystalline of tetragonal structure that was agreed with ASTM cart (14-0534).This crystallization is the result of annealing of the coat through soaking at temperature (400C) for about (15 minutes). Figures (2, 3) show XRD reflection peaks of ZrO_2 films doped with Al and Co respectively. These figures illustrate main changes in structural parameters of doped films. The structure remains tetragonal, which means that there is no effect of doping on ZrO_2 film structure [19], however doping results in some variation in dominant orientation, this result is obtained by other publishers [20]. Tables (2, 3, and 4) present XRD parameters for pure ZrO_2 film, doped with Al, and with Co respectively. They show that the films are characterized by lower values of (2θ) of peaks as compared with that indicated by ASTM cards. These shifts may lead to microtension stresses and result in larger values of lattice constants especially in a-lattice parameter as shown in table (4).These variations may also result in large values of lattice mismatch as it is seen in table (7).C-lattice parameter has, otherwise, little difference from that shown in ASTM standard and is varied with substrates temperature [21].Peak intensities and d-space of maximal peaks also showed some differences from that of ASTM standards (the value of d-space in ASTM standard is 2.948 A).

Table (6) shows the texture coefficients of coated samples with pure and doped ZrO_2 films. The average lower value of Tc for the plane (220) about 0.8 .This means that this is the preferable plane of ZrO_2 film growth and this result is agreed with other researchers [20,21] . Lattice mismatch, lattice strains, and grain size for the coated films were listed in table (7). The average value for pure and doped ZrO2 films was about (63.8%). A higher or lower lattice mismatch may be produced if a thin layer of another oxide of different a-parameter is deposited.

Al reduces lattice strains in doped ZrO_2 films and increases their grain size as shown in table (7) .This behavior is not seen if the film is doped with Co, this may be due to the atomic radii of the dope elements where Al atoms take the interstitial positions and Co atoms take the intermediate positions in ZrO_2 films [13]. FOUTO and KODAS prepared ZrO_2 films by using gas-phase process and find that it has tetragonal structure with average grain diameter of (20 nm) [10,22] .

The relation between grain size and roughness of coated films is shown in Figure (4).It is seen that there is direct linear relation between them.Figure (5) gives the relation between rate of deposition of pure ZrO_2 films and distance between spraying nozzle and substrate at different substrate temperatures. The best results were obtained when the distance was (15 cm) and the temperature was (400°C). These parameters were also adapted for spraying the doped films by Al or Co.

Variation of apparent density of pure and doped films with substrate temperatures is shown in Figure (6).Doping increases the density, especially doping with Co. The optimum substrate temperature was (400°C).Igaku prepared pure ZrO_2 film on Si substrate and obtained film density of (5.233 g/cm^3) [23,24].

Figure (7) illustrates the relation between the open pores in pure and doped ZrO2 films on steel substrate and substrate temperatures. It is shown that porosity of films is decreased with doping; especially with Co doping .lower porosity is also obtained at temperature of (400°C).SEM examinations give the same results as shown in figures (9, 10, 11).Jingyu studied nanostructured ZrO_2 coatings which was prepared by wet- chemical deposition followed by thermal processing. He noticed pores of (10 nm diameter) [2, 25].

The topographies of bare steels and that coated with pure and doped ZrO_2 films, obtained by SEM at different magnifications are shown in Figures, from (8) to (11). Figure (8) shows some defects on the surface of steel while the coated surface by pure ZrO_2 contains some pits as shown in higher magnification (X 1500) in figure (9). The variation of these pits (pores) was discussed in figure (7). Figures (10, 11) show the topographies of doped films with Al and Co respectively. There are no pits (pores) seen here and no other oxides are detected in these surfaces .These results have some agreements with other publishers [26]. These appearances may have an important influence on surface properties as compared with pure ZrO_2 films.

Conclusions

The main conclusion of this research are:

1-It is possible to prepare pure and doped ZrO_2 coat by spray pyrolysis method on glass and stainless steel 304 substrates .

2-Doping ZrO_2 coat with Co and Al decreases internal microstresses and microstrains .The doping with Co has the major effect.

3- ZrO_2 the only oxides has been detected during spraying ,and this give use perfect percentage of doping.

4-Doping ZrO_2 with Al or Co increases the coats density,and the highest density is obtained by doping with Co.

5-Open porosity of ZrO_2 coats were decreased with doping, and lowest open porosities were also observed by doping with Co.

6- The best spraying parameters for ZrO_2 deposition are :spray distance between nozzle and substrate (15 cm), and the substrate temperature is at(400Cº).

References

[1]M. KRZYZAK**,** G.HEINZ, Improvement of Enamel Surfaces by Sol-Gel Coating, "The International Enamellers Institute"(2006)4.

[2] K. CHOPRA, S. MAJOR and D. PANDYA, Transparent Conductors Films," Thin Solid Films", Vol.102 (1983) ,p1.

[3] L. MAISSEL , "Handbook of Thin Film Technology", McGraw-Hill, New York, 1970, Ch. 18.

[4]M. ADAMS, Applications of Zirconium Oxide, ZrO2 coats "Accuratus",2005.

[5]H.KON., Coating Materials News, "Technical Publications",Volume15Issue2 June, 2005.

[6]S.CHEFFING,C.CAMILLE" Properties of a Multilayer Coating for Applications in High Level Waste Packaging", Master's Thesis, NCSU LIBRARIES, 2005.

[7]F.RAYNER, G. BRUCE,." Spectroscopic Investigation of Local Bonding in Zirconium Silicate High-k Dielectric Alloys for Advanced Microelectronic Applications", PhD, NCSU LIBRARIES, 2002.

[8] D.NGUYENM. ,Amorphous Al_2O_3 and Al_2O_3-ZrO_2 Films by Spray Pyrolysis,"Thin Solid Films"135(1986) L19-L21.

[9] J.WACHTMAN "Ceramic Films And Coatings" ,WILLIAM ANDREW, (2008) .

[10] G. Fotou, T. Kodas, Coating Titania Aerosol Particles with ZrO_2, Al_2O_3/ZrO_2 and SiO_2/ZrO_2 in a Gas-Phase Process ," Aerosol Science and Technology", Vol. 33, No. 6, 11 December 2000 , pp. 557-571(15) .

[11] R.WEAST ,"CRC Handbook of Chemistry and Physics" ,CRC press 1985.

[12] R. AL-OBOUSY, Study the Effect of the Doping in Some physical properties of ZnO thin film ,MSc Thesis, Applied Science Department,University of Technology,2005.

[13] Y. SIROTIN AND M. SHASKOLSKAYA ,"Fundamentals of Crystal Physics" (Mir Publishers, Moscow 1982).

[14] B.JOSEPH,P.K. MANOJ, V.K .VAIDYAN, Studies on Preparation and Characterization of Indium Doped Zinc Oxide Films by Chemical Spray Deposition," Bull.Mater.Sci."Vol.28,(5)(2005)4 87.

[15] Y. LU, M. REN, Z. MAI, The effects of the thermal annealing on ZnO thin films grown by pulsed

laser deposition," J. Appl. Phys.", Vol.88 (1) (2000) 498.
[16] T. OBATA, K. KOMEDA, Structural Characterization of $Si_{0.7}$ $Ge_{0.3}$ Layers Grown on Si (001) Substrates By Molecular Beam Epitaxy ," J. Appl. Phys.", Vol.81 (1997) 199.
[17] E. TURNEN, Ari Hirvonen, Application of HVOF Techniques for Spraying of Ceramic Coatings, "J. of Materials on Line ",Vol. 3 Dec. 2007.
[18] ASTM(D3258-04).
[19] R.H FRENCH., S. GLASS, Properties of R.F Reactively Sputtered Cu-doped ZrO_2."J.of Physical Review B",Vol.49,5133 -42(1994).
[20] S. MAJOR, A. BANERJEE and K. CHOPRA, High transparent & conductive ZnO:In films," Thin Solid Films", Vol.108 (1983) 333.
[21] S. TAKADA ,Relation Between Optical Property and Crystallinity of ZrO_2 Thin Films Prepared by R.F. Magnetron Sputtering , J. Appl. Phys., Vol. 73 (10) (1993) 4739.
[22] C. MITCHELL, Decorative hard Coatings,"Technical Publications", Vol.8,Issue1(1998).
[23] R.IGAKU, Evaluation of the structure of a high-k gate insulation thin film"Smart Lab Application",2008.
[24] S.JINGYU , Oxide nanoparticles and nanostructured coatings by wet chemical processing ," Materials Science and Engineering ", Ohio State University, 2006, 138p.
[25] S.ENGELHARD, H.Mark. , A Samina , S. Laxmikant V, Distribution of Oxygen Vacancies and Gadolinium Dopants in ZrO_2-CeO_2 Multi-Layer Films Grown on α-$Al2O_3$," Journal: Solid State Ionics", Vol.177(15-16):1299-1306; Journal Volume: 177; Journal Issue: 15-16.
[26] J. Delmonte," Fabrication of thin oxide films by combustion spray pyrolysis", Van Nastrand Reinhold Com.2000.

Table (1) Chemical composition of steel 304

Element	304(Austenitic) Standard	304(Austenitic)Measured
Carbon	0.08	0.08
Manganese	2.00	2.1
Phosphorus	0.045	0.05
Sulfur	0.03	0.04
Silicon	1.00	0.9
Chromium	18.00-20.00	18
Nickel	8.00-10.50	8.01
Iron	Balance	Balance

Table(2)Result of XRD of pure ZrO_2film.

$2\theta_{ASTM}$	$2\theta_M$	(hkl)plane	I_{ASTM}%	I_M%	d(Å)
30.283	30.13	111	100	100	2.9634
34.687	34.5	002	20	16.8	2.59744
35.278	35.11	200	60	36	2.5538
50.553	50.2	220	100	83	1.8157
60.240	60.00	311	80	76.8	1.5405

Table(3)Result of XRD of ZrO_2:Al film.

$2\theta_{ASTM}$	$2\theta_M$	(hkl)plane	I_{ASTM}%	I_M%	d(Å)
30.283	30.18	111	100	100	2.958
34.687	34.6	002	20	16.3	2.59016
35.278	35.2	200	60	54.09	2.547
50.553	50.3	220	100	67.21	1.812
60.240	60.1	311	80	53.27	0.888

Table(4)Result of XRD of ZrO_2:Co film.

$2\theta_{ASTM}$	$2\theta_M$	(hkl)plane	I_{ASTM}%	I_M%	d(Å)
30.283	30.25	111	100	100	2.9519
34.687	34.7	002	20	15.32	2.5829
35.278	35.18	200	60	52.41	2.5487
50.553	50.4	220	100	65.32	1.809
60.240	60.2	311	80	53.22	1.5358
74.677	74.2	400	60	11.29	1.2769

Table (5) Lattice parameters of samples prepared at different conditions.

structure	a(nm)	c(nm)
ASTM cart(14-0534)	5.09	5.18
Pure ZrO_2	5.89	5.194
ZrO_2:Al	5.882	5.1803
ZrO_2:Co	5.8859	5.1658

Table (6) The texture coefficient of samples prepared at different conditions.

hkl	Tc(ZnO_2)	Tc(ZnO_2:Al)	Tc(ZnO_2:Co)
111	1.181	1.232	1.205
002	0.992	1.005	0.923
200	0.708	1.111	1.053
220	0.982	0.828	0.787
311	1.134	0.821	0.802
400	--	--	0.227

Table (7) Same calculated parameters of films.

structure	L.M%	%δ	g.s(nm)
Pure ZrO_2	0.638	0.27	148.6
ZrO_2:Al	0.637	0.058	185.8
ZrO_2:Co	0.637	0.27	165.4

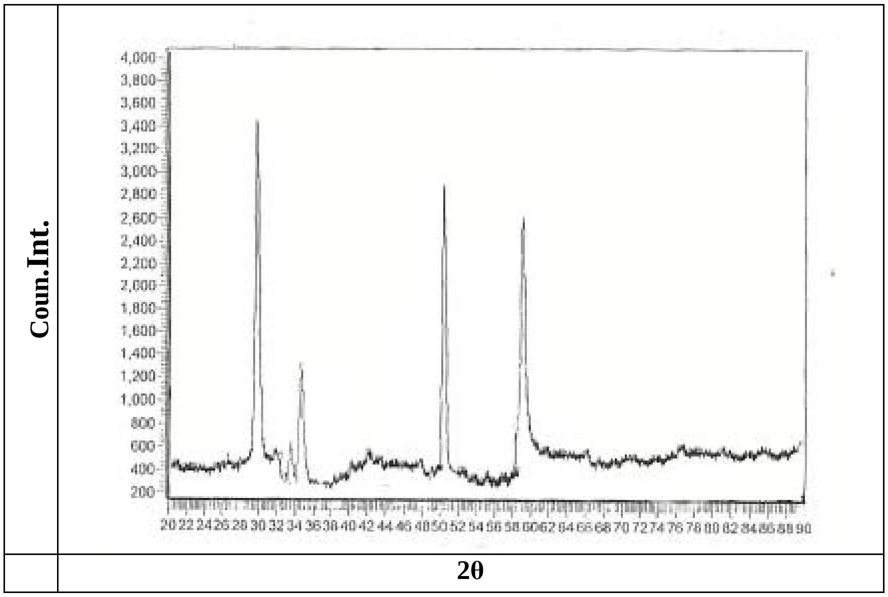


Figure (1) XRD spectra of pure ZrO_2film.

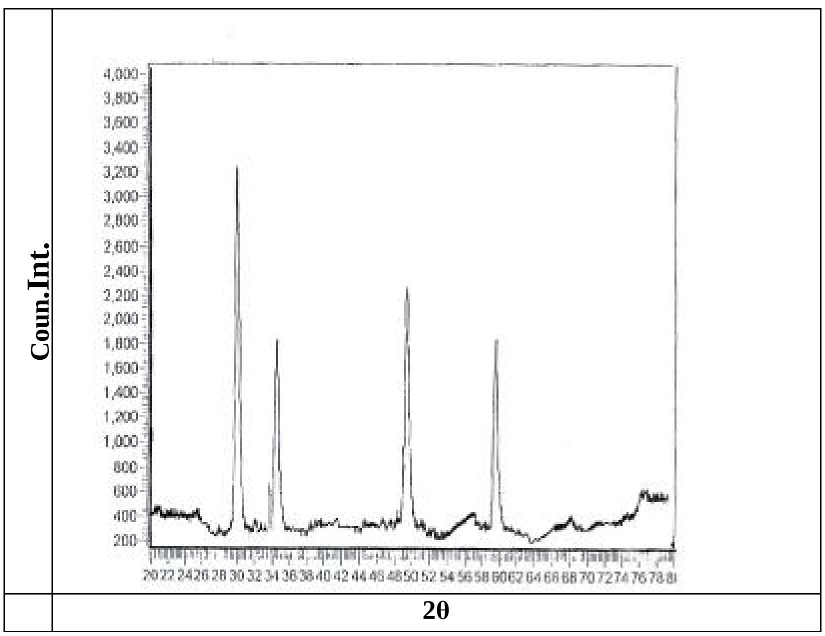


Figure (2) XRD spectra of ZrO_2film doped with Al(5wt%)

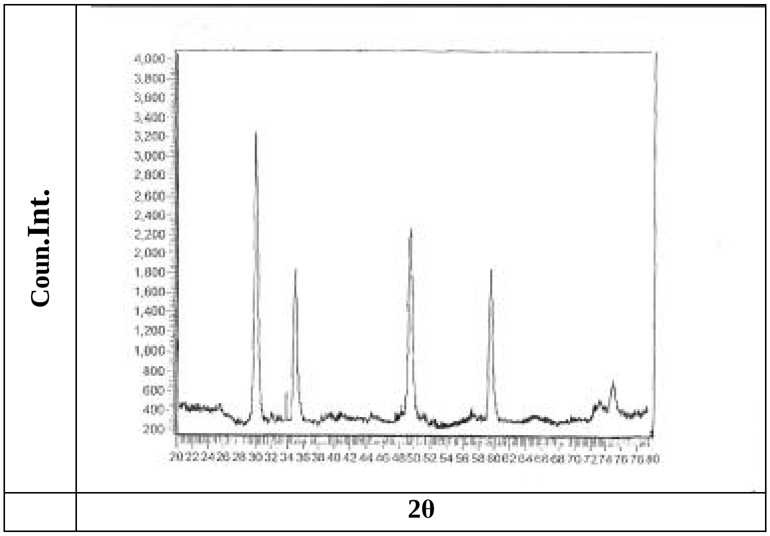


Figure (3) XRD spectra of ZrO_2film doped with Co(5wt%).

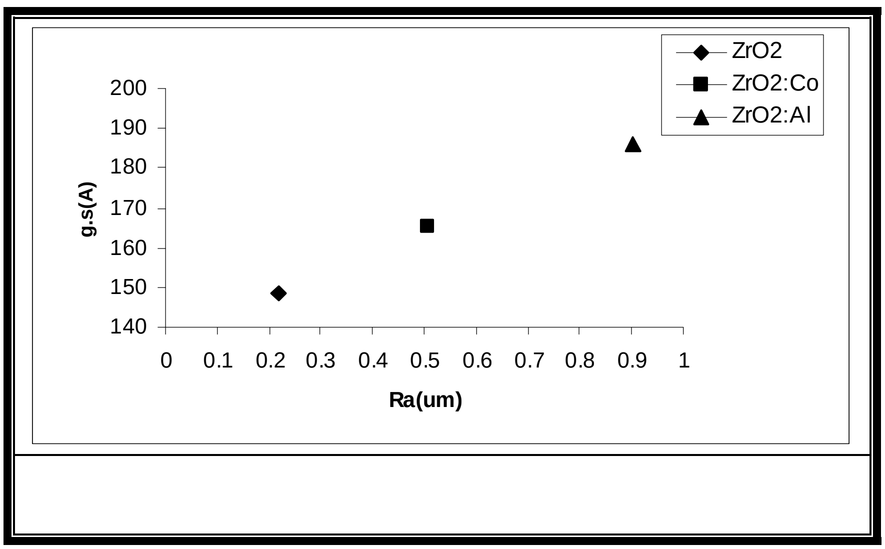


Figure (4)Relation between grain size and surface roughness.

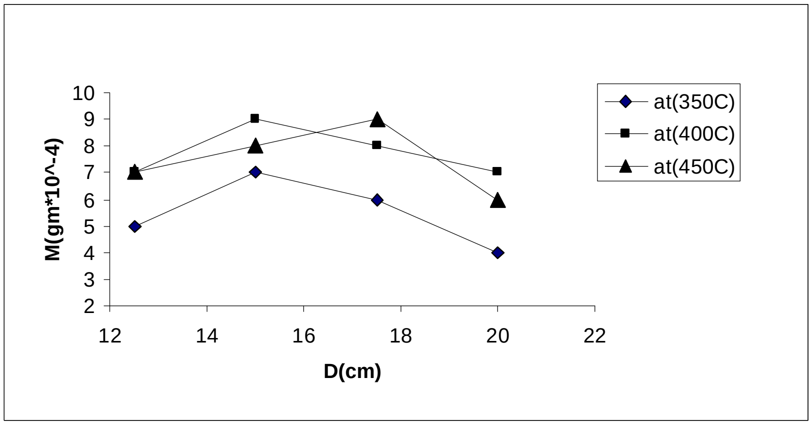


Figure (5) Variation rate of deposition and distance between spray nozzle and substrate at different temperature.

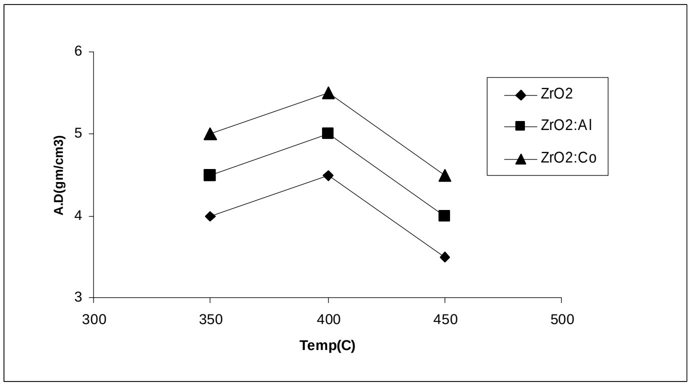


Figure (6) Variation of apparent density of ZrO_2 films and substrate temperature.

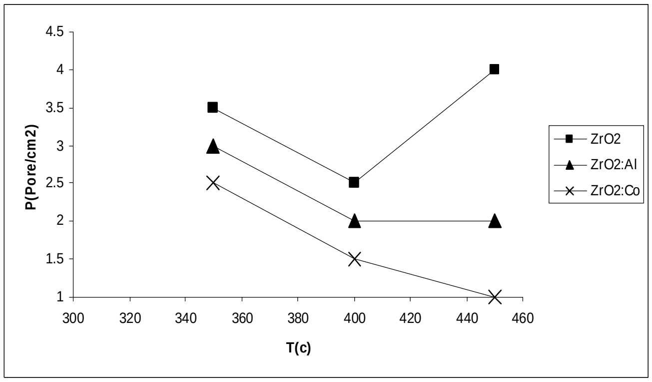


Figure (7) Open pores in ZrO_2 film on stainless steel304 with spraying temperature.

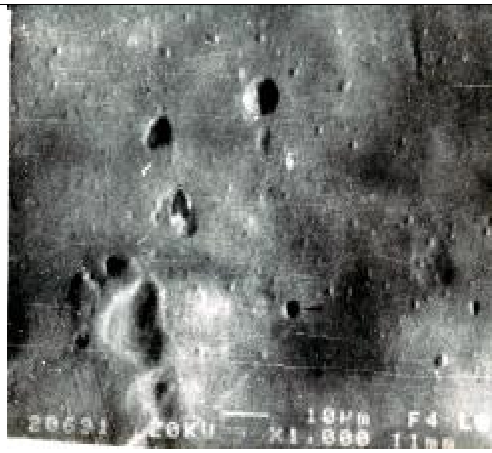
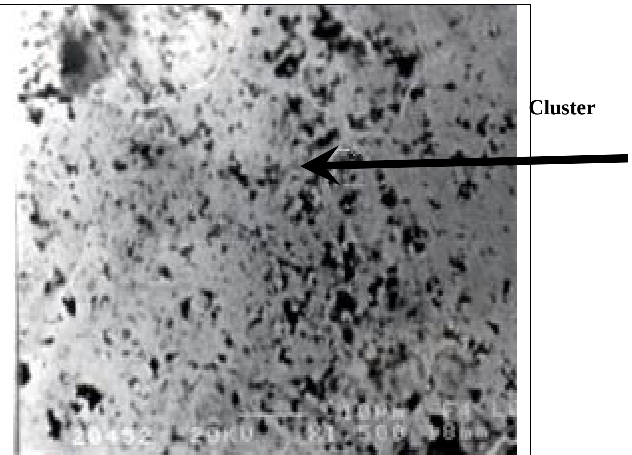
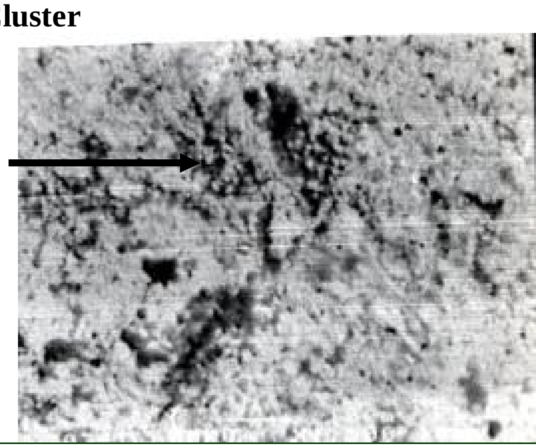


Figure (8) 304 stainless steel substrate (X1000) .



Figure(9) Pure ZrO_2film (X1500).



Figure(10)SEM of ZrO_2:Al film (X1500).

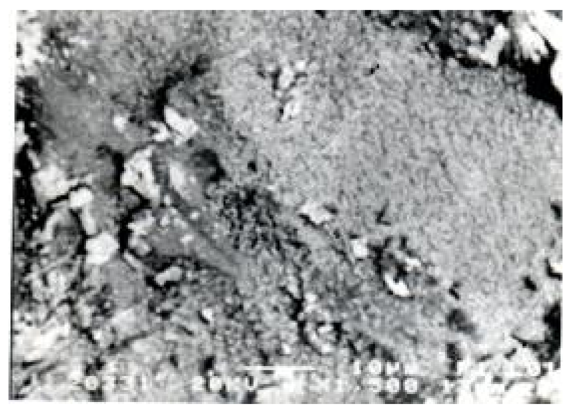


Figure (11) SEM of ZrO_2:Co film (X1500).