The Iraqi Journal For Mechanical And Material Engineering, Vol.20, No3,Sept. 2020

PREPARATION AND CHARACTERIZATION OF TiO_2-ZrO_2 COATING PREPARED BY SOL-GEL SPIN METHOD

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ABSTRACT

Spin coating is used in various industrial and engineering applications, inducing the producing of thin films within nano-scale boundaries. In industrial processes, different substrates can be subjected to spin coatings, for example, micro microfilms, etc. In this research, Titanium tetra-isoperopoxide (TTIP) is used in the preparing of composite coatings by sol-gel spin method. The structure and chemical compositions of the composite coatings are studied using X-ray, SEM and EDS methods. The XRD pattern clearly shows the additions of 2% and 4% ZrO_2 and their effects on the morphology and crystalline structure of titanium oxide, in addition; increasing the additives of ZrO_2 in TiO_2 films improves the intensity of diffraction peaks. The optical photographs show the microstructure of TiO_2 doped 2% and 4% ZrO_2 crystallization beads film measured to be 100.81 µm and TiO_2 doped with (2 and 4% ZrO_2) films are approximately 122.8813 µm in thickness. The SEM results of pure sol-gel TiO_2 are relatively smooth, almost uniform dispersion of ZrO_2 particles occurs in the matrix. The EDX results show the presence of the Ti and high amounts of Zr in the structure of the matrix. Coating hardness measurements exceed 70% with doped TiO_2 and it increases with increasing the amount of zirconia.

Keywords: TTIP, spin coating, TiO_2–ZrO_2 composite coating, sol-gel.

تحضير وتوصيف طلاء TiO_2-ZrO_2 باستخدام المحلول الهلامي بواسطة الطلاء بالدوران

هناء عزيز سميج شيماء مهدي صالح ليث وضاح اسماعيل

الخلاصة

يستخدم طلاء الدوران في التطبيقات الهندسية والصناعية المختلفة، مما يؤدي إلى إنتاج أفلام رقيقة داخل حدود النطاق النانوي. يمكن أن تتعرض معظم الركائز لطلاءات الدوران، على سبيل المثال ، الميكروفيلم الصغير، إلخ. في هذا البحث، تم استخدام Titanium tetra-isopropoxide (TTIP) في تحضير الطلاء المركب باستخدام المحلول الهلامي بواسطة الطلاء الدوراني. تم فحص البنية والتركيب الكيميائي للطلاء المركب باستخدام طرق الفحص X-ray، SEM، كذلك EDS. نموذج XRD يبين الإضافات التي تحتوي على 2٪ و 4٪ من ZrO_2 وتأثيراتها على التشكل والبنية البلورية لأكسيد التيتانيوم ، بالإضافة إلى ذلك؛ زيادة إضافات ZrO_2 في أغشية TiO2 تعمل على تحسين كثافة قمم الحيود. تم تحليل البنية المجهرية الى TiO_2 2٪ و 4٪ ZrO_2 وكان قياس الطبقة البلورية 100.81 ميكرون، اما بالنسبة لاغشية الى TiO_2 مع (2 و 4٪ ZrO_2) حوالي 122.8813 ميكرون. نتائج فحص ال SEM الخاصة بـالسائل الهلامي ل TiO_2 ناعمة نسبيًا ، ويحدث تشتت منتظم تقريبًا لجزيئات ZrO_2. تظهر نتائج EDX وجود Ti والكميات العالية من Zr. قياسات صلابة الطلاء تتجاوز 70٪ مع TiO_2، ويزيد مع زيادة كمية الزركونيا.

Received : 26-9-2019
Accepted :15-8-2020

INTRODUCTION

A protective coating is a material layer formed synthetically naturally and it deposited artificially on the surface. It acts as a barrier between the component and the influences of the aggressive atmospheric environment, it is also used for corrosion protection. Globally, it is well known to be an attractive means to reduce the damage of real components at a significant rate by acting as the first line of defense. Recently, many researchers have developed various methods to apply Titanium Dioxid (TiO_2) coatings on various substrates [Mohammeda et al., 2018]. Sol-gel technique is a chemical process to the synthesis of inorganic or metal oxide materials such as Titanium dioxide. It used for synthesis nanomaterials, and bulk materials, which form a gel available for use in different coating methods such as dip and spin coatings. It is convenient for nano, thin, and thick film deposition on substrates at low temperatures [Roy, 1987; Pierre, 2013]. Stainless steel as a substrate is widely used in different industrial applications because of its good properties such as mechanical, corrosive, etc. However, they have the tendency to corrosion in the environment of halide ions. There are challenges in the spin coating process because of the complex coupling of coating solvent evaporation. Two types of sol-gel processes depending on the metal precursor type of titanium can be particularly used to produce TiO_2 semiconductors [Napper et al., 1971; Hussain et al., 2017]. Sol-gel dip-coating technique can provide corrosion protection performance and it can produce a thick coating. Due to the thick coating, the possibility to get a crack thin film is high. Therefore, the aim of this paper is the preparation and investigation of the composite coating base of TiO_2 with ZrO_2 films at different percentages by sol-gel spin coating technique and studying the structure and mechanical properties.

EXPERIMENTS

Materials

Low carbon steel was used in this work. The chemical composition of steel alloy was (0.2 Si, 0.122 C, 0.40 Mn, and 0.05 Cr) which was carried out in the ministry of science and technology-Baghdad using the atomic absorption technique. Square specimens with a size of 10×5×4 mm were used in this study. The open surfaces of the specimens were polished by silicon carbide papers which were used to give uniform shapes of the sample's surface, the polishing used 400, 500, 600 and 800 grit of SiC sheets. To ensure scratch-free finish surface polishing with coarse diamond, the samples were cleaned to remove any contamination on the surfaces with methanol liquid. Finally, the samples were rinsed in deionized water and air-dried.

Sol-gel TiO_2 film

In the Sol-gel spin composite coating method, Titanium tetra-isoperopoxide (Aldrich 99.99%) was used as a base material and nitric acid. A mixture of Titanium tetra-isoperopoxide (10 ml) and ethanol (5 ml) with water (100 ml) is synthesized, Then, the nitric acid (1 ml) was added to the mixture. This leads to obtaining sol after 4 hours at 80C° under energetic moving using a magnetic stirrer, a milky solution was produced. The mixture was aged for 48 hours at room temperature in the air. Coatings were conducted by the spin-coating method.

Composite coating preparation

Spin coater (mode 410, origin Taiwan) was used to perform a coating with a uniform thin films to flat energetic moving substrates. The composition of the coating mixture from TiO_2 with ZrO_2 provided by BDH laboratory , powder with purity of 99.9% (50 μm) was applied to the spin coater center of the substrate at low speed. Then, the samples were rotated at 500 rpm at 2 sec. Fig. 1 shows the spin coater device located in the Corrosion Laboratory, Material Engineering Department, University of Technology. The thickness of the coating depends on the concentration and viscosity of the mixture. After the coating process, the coated specimens were dried in a furnace at 37^0 C for 5 hr. The specimens were weighed before and after coating to get the coating weight.

Characterization of composite coating

The morphology of structure and S distribution of the elemental composition were investigated using the TESSCAN VEGA 3 scanning electron microscope (SEM and EDX) (The VEGA Easy Probe) has higher magnification, high depth of field, greater resolution, compositional and crystallographic information, at 30 KV. It was used to analyze the surface morphology of coated specimens. The phase analysis of titanium oxide (TiO_2) and the composition of the coatings were obtained using the Phillips Norelco X-Ray, the diffractometer operates with CuKα (λ= 1.54178 Å) radiation at 30.0 mA with 40.0 KV end degree of 10-80 deg. The hardness exam was done by using the Vickers macro hardness tester (Beijing Time High Technology LTD Time Group INC) by applying a (50 gram as Hv 50) load. The test is adjusted for 20 sec by ply four value an indentation. The value of Vickers hardness was measured by average diametrical of this indent.

RESULTS AND DISCUSSION

The composition of TiO_2 films synthesized was determined through the preparation of TiO_2 from sol-gel spin coating. Fig. 2 shows the XRD pattern of TiO_2 xerogels of pure TiO_2 films. Fig. 3 shows the 4% ZrO_2-doped TiO_2. The XRD pattern evolution of TiO_2 xerogel after the evaporation 24 hr shows an amorphous phase [Brinker et al., 2013; Bukhari et al., 2019]. This analysis of the xerogel doped offers that the addition of 4% ZrO_2 no effect on titanium oxide morphology [Mdahfar et al., 2018; Kosmulskiet al., 2004]. The XRD patterns clearly shows that two main peak of films which corresponds to anatase (101), (110) and (220) planes. The peak corresponding to the rutile phase can be clearly seen in the films which have high intensity. The influence of doping with ZrO_2 is performed by a comparison between XRD patterns doped with 2 and 4% ZrO_2 as shown in Fig. 3. The thin films obtained showed characteristic peaks correspond to the crystallization of TiO_2 phases of the doped state are shifted to larger angles compared to the undoped one and can be clear which has high intensity compared to the prior sample. The addition of 2% and 4% ZrO_2 affects titanium oxide morphology shows a crystalline structure; besides, the increasing of the addition of ZrO_2 in TiO_2 films improves the intensity of diffraction peaks [Napper, 1977; Abbas et al., 2019]. The pure TiO_2 peaks have shifted towards the higher angle values with the addition of ZrO_2 particle, this analysis of the TiO_2 gel exhibits the addition of 4% ZrO_2 would be largely sufficient to form particles of crystallizes of anatase. Fig. 4 shows the coating thickness by optical microscope photographs of the specimens at magnification 40X. Fig. 4a is for a crystalline TiO_2 film. Figs. 4b and 4c show the microstructure of TiO_2 doped 2 and 4% ZrO_2, more crystallization beads of coating structure were formed on the steel surface. Computerized optical microscope shows the average coating thickness to be 100.81 μm and TiO_2 doped with 2 and 4% ZrO_2 films are approximately 122.8813 μm thickness of the coating. Fig. 5 shows an optical microscope of coating which revealed that better hemocompatibility with thickness increases. An important part of the work is the microstructure study of single pure TiO_2 and the additives ZrO_2 in a percentage weight of 2% and 4%. This test was done to observe the phase distribution of the additives in ZrO_2 matrix at the same experimental conditions and the changes in the shape of the ceramic particles to be observed, the porosity and compositional variations of modified against unmodified coating are also observed. Fig. 6A shows the microstructure of pure sol-gel TiO_2 which is relatively smooth, clean and formed of regular lines. The light phase and dark phase are appeared, whereas the microstructure in the Figs. 6B and 6C show almost a uniform distribution of ZrO_2 particles into the matrix with a full dispersion in TiO_2 matrix to be dense.

There is no separated without forming any agglomeration or porosity in the composite coating from the TiO_2 matrix. Thus, coating surfaces of TiO_2 with ZrO_2 are more systematic without of voids and porosity or with close of structure. High densification due to high homogeneous of the specimens after applied of coating resulting in more coalescence between particles. There is a reduction in the porosity and increasing adhesive surface and continuous with a best homogenous mixture of TiO_2 with ZrO_2 particles, the densification leads to the bushy composite coating at thin ZrO_2 Peed implanted within a dense base on the surface of the substrate. Fig. 7A shows the EDX results show the presence of mostly Ti (27.14%) in the structure of the matrix. Higher Zr (0.8% and 4.66%) were detected along with Ti (27.14%) and (34.08%) respectively. Fig. 7B shows the EDX morphology analysis of composite coatings sol-gel spin ceramic coated at interface, which indicates the presence of mostly Ti (27.14%) in the matrix with higher amounts of Zr (0.8% and 4.66%) were detected along with Ti (27.14%) and (34.08%) respectively [Xu et al., 1994; Feinle et al., 2016]. The values of surface roughness (Ra) for all coatings are shown in Fig. 8. The results show that the morphology of coating surface is smoother and it appears a uniform distribution and fine sizes of structure leading to boosted average diameter and roughness (Ra) values measured of particles which is shown in Fig. 9. It is mainly related to the first coating TiO_2 sites for deposition and it seems that the roughness of the films is strongly affected by coating sequences. This means that the preferred of TiO_2 particles were determined by surface tip. However, in the second coating, the substrate surface was covered with TiO_2 particles. Fig. 10 shows the Vickers microhardness behavior of pure TiO_2 and with ZrO_2 composite coating. The values of hardness of the coatings were increased as the content of the ceramic powder increases. The enhancement of hardness is relatively above 70% for doped TiO_2, it increases with increasing the amount of zirconia [Hong, 2006; Zhang et al., 2009]. The increasing hardness value is due to the morphology and structure of composite coating which is smoother and no presence of defects. It has a fine structure with a homogenous in distribution which results in boost values of roughness (Ra) this affects the hardness behaviors, especially for sol-gel spin coating methods.

CONCLUSIONS

- Addition of 2% and 4% ZrO_2 effect on titanium oxide morphology and crystalline structure, besides, increasing with add ZrO_2 in TiO_2 films improves the intensity of diffraction peaks.
- Microstructure of TiO_2 doped ZrO_2 more crystallization beads film prepared by sol gel spin coating was formed on the steel substrate.
- Structure of TiO_2 with ZrO_2 ceramic coating specimens is high densification due to high homogeneous of the specimens after applied of coating resulting in more coalescence between particles, increasing adhesive surface and continuous with a best homogenous mixture of TiO_2 with ZrO_2 particles.
- Coatings hardness is approaching with doped TiO_2 above 70%, it increases with the increasing amount of zirconia due to the no presence of defects or cracks and the surface morphology is smoother and has fine sizes leading to enhance roughness values (Ra).

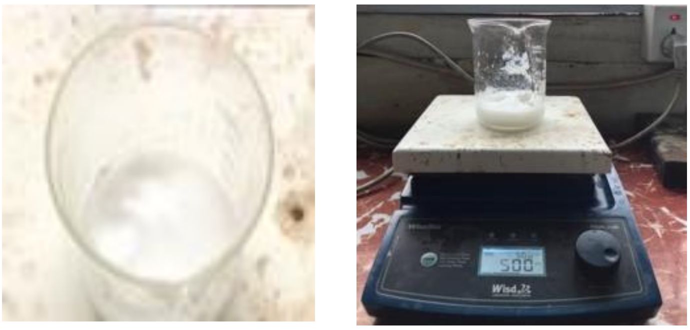


Fig.1 preparation of sol gel TiO_2 coating

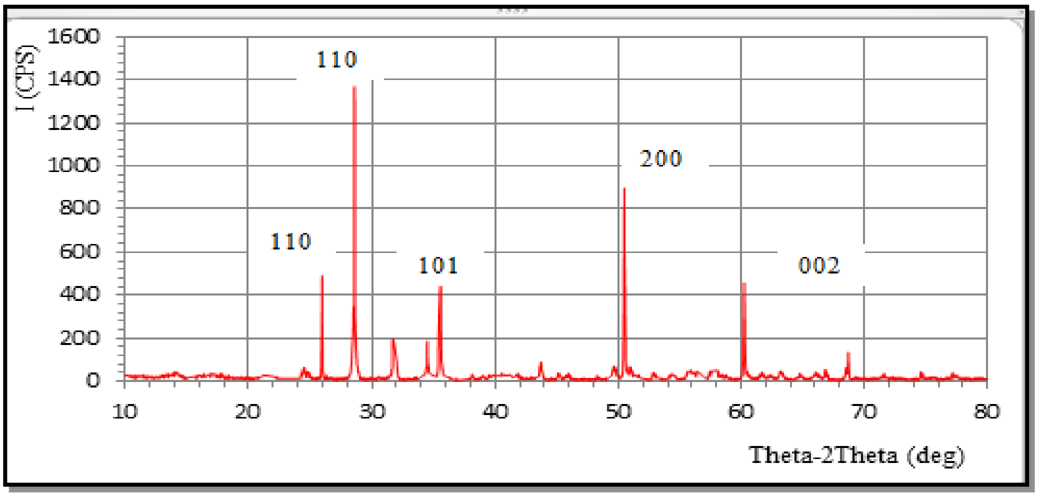


Fig. 2 X-ray patterns of pure coatings

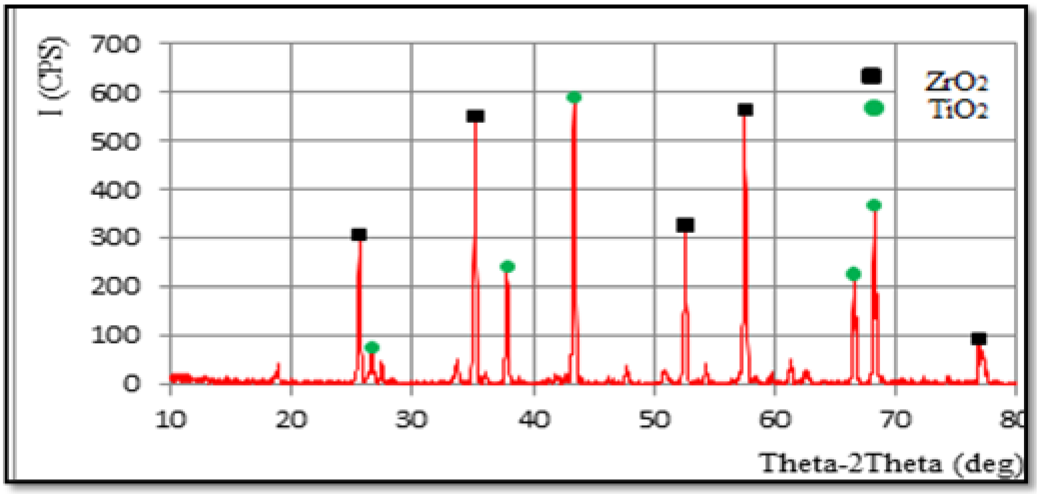


Fig. 3 X-ray patterns of 4% doped coatings

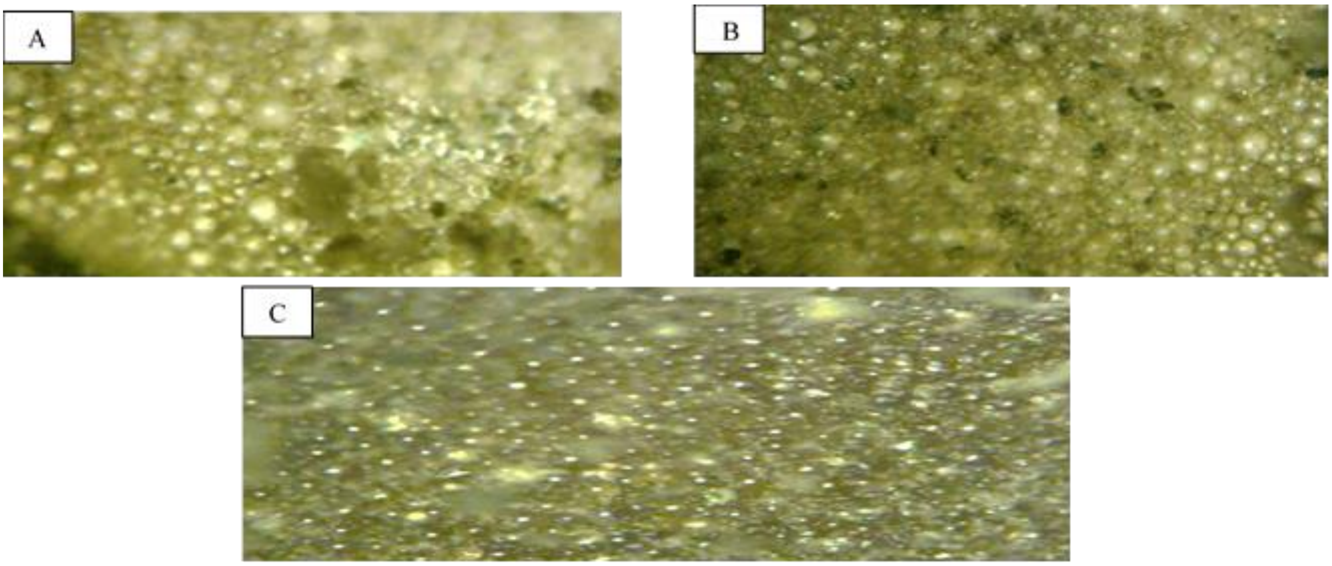


Fig. 4 Typical optical microscope image:(A) TiO_2, (B) TiO_2 doped 2% ZrO_2 coating and (C) TiO_2 doped 4% ZrO_2 coating.

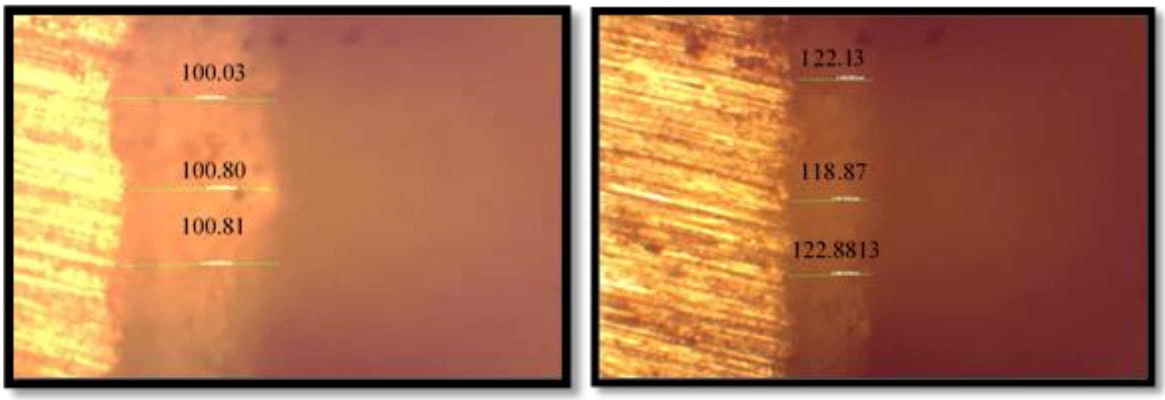
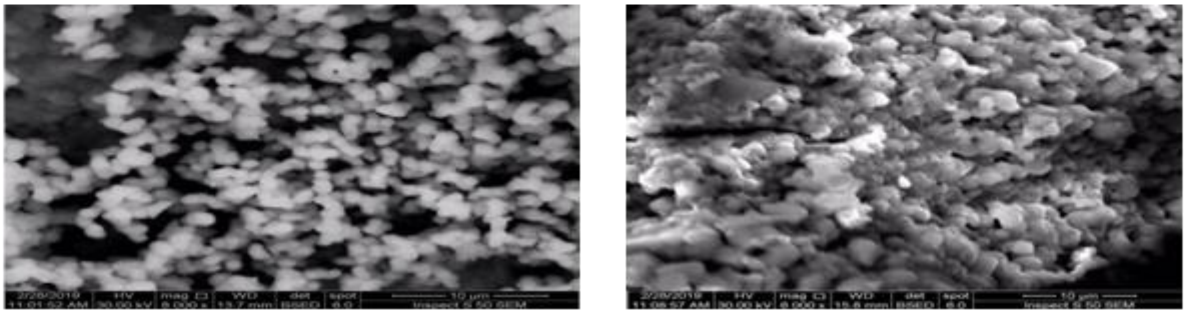
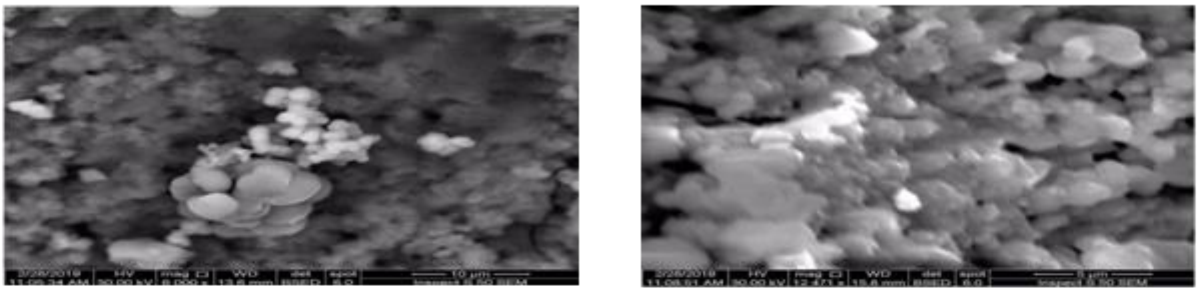


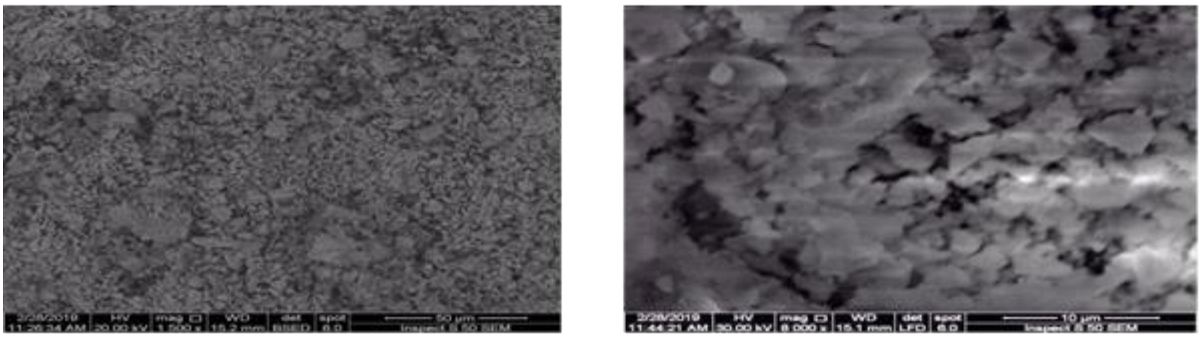
Fig. 5 Optical microscope of coating thickness.



(A)

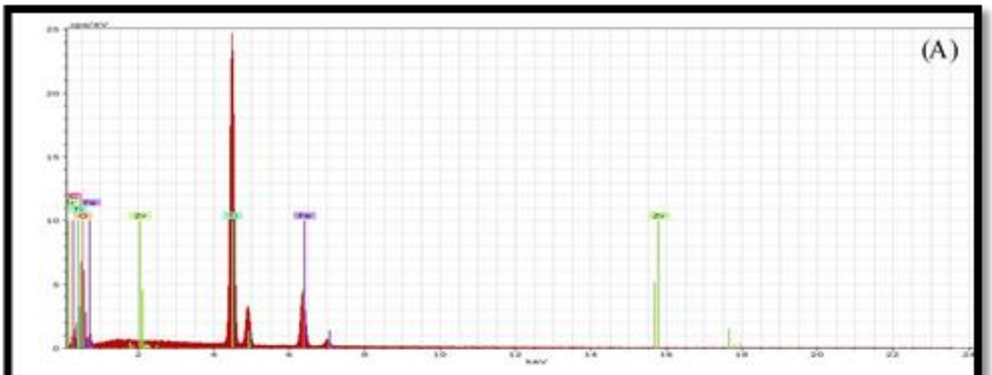


(B)



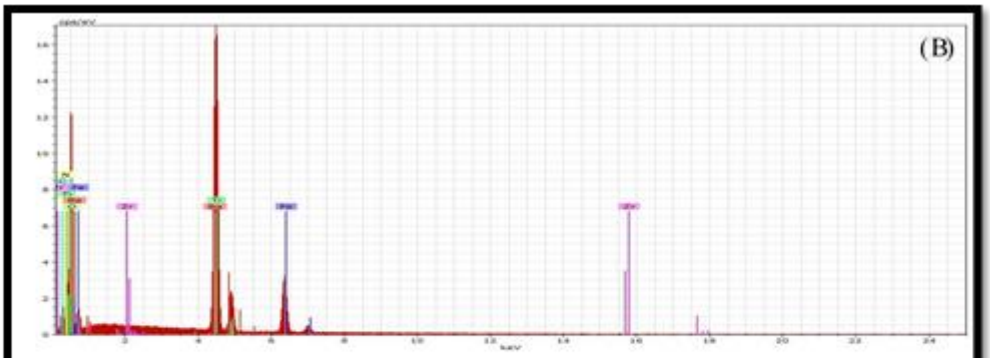
(C)

Fig. 6 Surface morophology coatings. (A) Pure coatings, (B) 2% doped coatings, and (C) 4% doped coatings.



Spectrum: Acquisition 2293

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
O	8	K-series	46.39	47.48	66.63	7.68
Ti	22	K-series	34.08	34.88	16.36	1.00
Fe	26	K-series	10.44	10.68	4.29	0.34
C	6	K-series	6.62	6.78	12.67	1.74
Zr	40	K-series	0.18	0.18	0.04	0.09
		Total:	97.70	100.00	100.00	



Spectrum: Acquisition 2294

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
O	8	K-series	51.21	37.91	63.23	8.74
Ba	56	L-series	32.05	23.72	4.61	1.00
Ti	22	K-series	27.14	20.09	11.20	0.85
Fe	26	K-series	9.90	7.33	3.50	0.37
C	6	K-series	9.23	6.83	15.18	2.65
Zr	40	K-series	4.66	3.45	1.01	0.64
N	7	K-series	0.90	0.67	1.27	0.66
		Total:	135.09	100.00	100.00	

Fig. 7 EDX morphology for the composite coatings sol-gel spin specimens on metal substrate

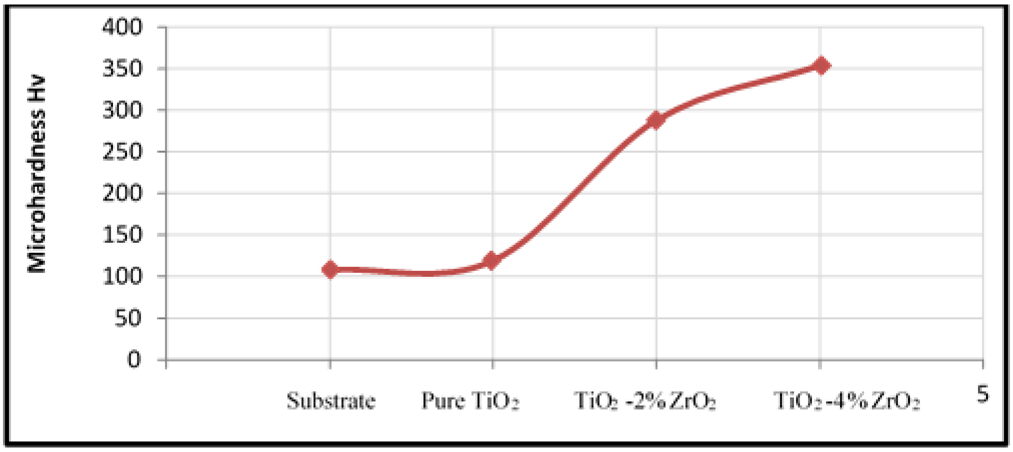


Fig. 8 Surface roughness (Ra) of coatings

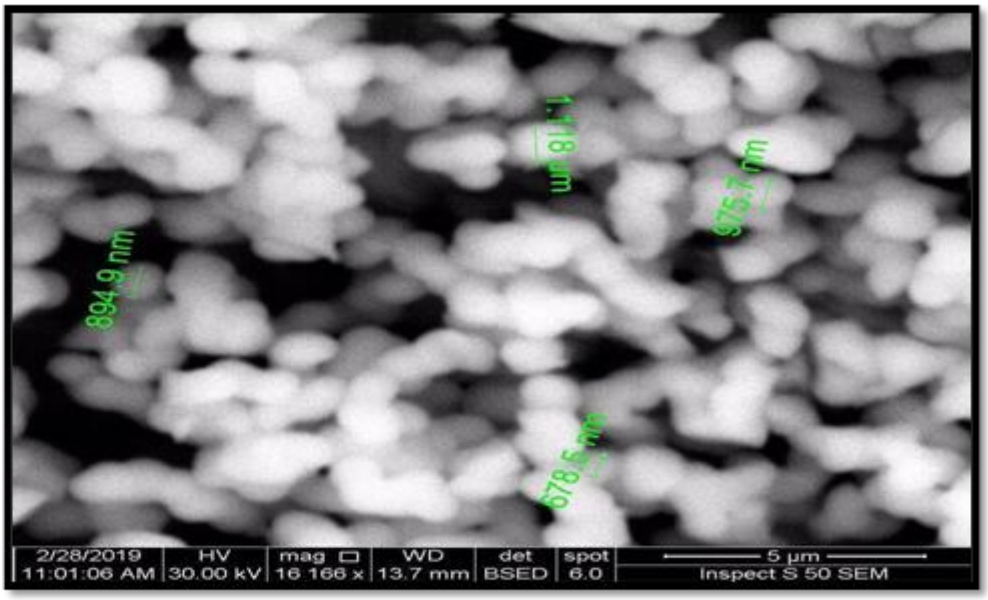


Fig. 9 Average diameter of ceramic coating by sol gel spin coating

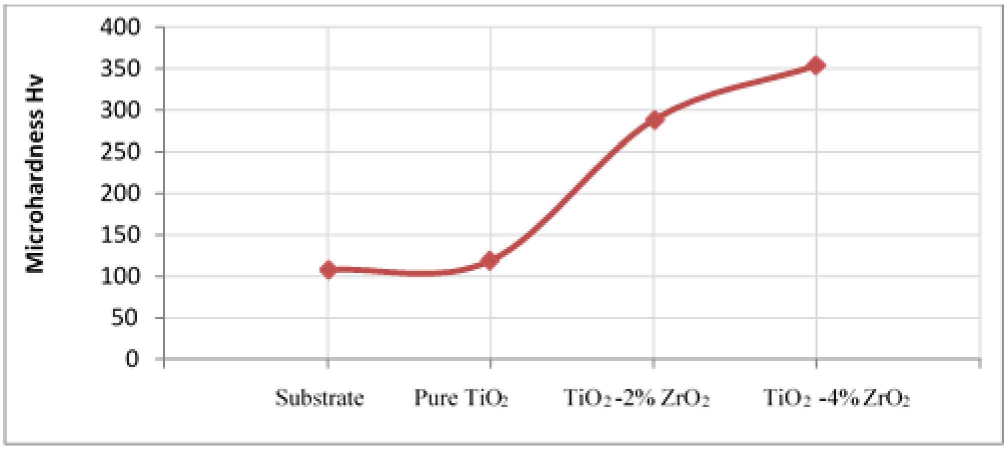


Fig. 10 Vickers microhardness of ceramic coating by sol gel spin coating

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