Study of Hardness ,Wear and Corrosion Resistance of ZrO_2Ceramic Coats Prepared by Spray Pyrolysis Method

Dr.Ali H.Ataiwi ,Dr.Alaa A. Abdul-Hamead
Ataiwiali1@yahoo.com,Alaalani2005@yahoo.com
Materials Eng. Dept ., University of technology

ABSTRACT

In the present work pure and doped ZrO_2 with (Al and Co 5wt%) thin film has been deposited on stainless steel 304 substrates by spray pyrolysis technique .The film microhardness, wear resistance, and the corrosion at different acids and alkaline are studied . The results are proved that the microhardness and wear resistance were improved after doping specially with (Co).The microhardness of the films has been improved from(927 Kg/mm^2) for pure ZrO_2film to(1095 Kg/mm^2) 5 wt% of Co . Wear resistance has been improved from ($10*10^{-10}$ g/cm) for pure $ZrO_2$to (3.79 $*10^{-10}$ g/cm) after doping with Co. Loss of weight by corrosion was decreased after coating and doping .

Key word: spray pyrolysis, ZrO_2 *film*, microhardness, wear resistance, ceramic coats.

دراسة الصلادة و مقاومة البلى و مقاومة التأكل الكيمياوية لطلاءات الزركونيا ZrO_2السيراميكية المحضرة بطريقة الرش الكيماوي الحراري

د.علي حسين عتيوي د.الاء علاء الدين عبد الحميد

قسم هندسة المواد-الجامعة التكنلوجية

الخلاصة

في هذا البحث تم بطريقة الرش الكيميا ئي الحراري ترسيب أغشية من الزركونيا ZrO_2 النقية و الزركونيا المشابة بنوعين من المعادن وهي الالمنيوم و الكوبلت وبنسبة وزنيه بلغت (5 wt%) إلى الزركونيا على قواعد من الفولاذ304 المقاوم للصدأ .تم اولا دراسة الصلادة الدقيقة و مقاومة البلى بالإضافة إلى قياس معدل التاكل بطريقة فقدان الوزن في محاليل حامضية و قاعدية .أثبتت الفحوصات تحسنا ملحوظا في الصلادة الدقيقة و مقاومة البلى بعد الاشابة و خاصة الاغشية المشابة بالكوبلت ,حيث ازدادت الصلادة الدقيقة من (927 Kg/mm^2) للاغشية النقية الى (1095 Kg/mm^2 .أما مقاومة البلى فقد تحسنت بشكل كبير بعد ترسيب زركونيا من ($10*10^{-10}$ g/cm) الى ($3.79 *10^{-10}$ g/cm),بينماتناقصت قيمة الفقدان بالوزن بفعل التآكل بشكل كبير بعد الطلاء و الاشابة.

INTRODUCTION

Ceramic coatings can improve the chemical and mechanical durability of steel at higher temperature M. Krzyzak2006.Spray pyrolysis coating is a technology used to improve surface properties of a wide range of substrate materials, including glasses, ceramics, plastics and metals, K. CHOPRA *et al*. 1983, L. MAISSEL1970. Spray pyrolysis involves spraying of a solution, usually aqueous, containing soluble salts of the constituent atoms of the desired compounds onto heated substrates. The technique is very simple and is adaptable for mass production of large-area coatings for industrial applications. Doping can be easily achieved by this technique via adding the salt of the desired dopant into the solution.Different carrier gases are used in this technique (O_2, N_2, Ar or air). Thin oxide films 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,M. Adams2005, H.Kon2005, S.Cheffing2005, Rayner2002. D.NGUYENM 1986 prepared $ZrO_2$and Al_2O_3-ZrO_2 films prepared by spray pyrolysis by using $Zr(C_4H_9O)_4$ and studied the film by using XRD and SEM. The films were amorphous and after annealing at (550 Cº) became crystalline. Zircona is one of the most important thin oxide film materials because of their favorable dielectric properties, low thermal conductance and high wear and corrosion resistances, D.NGUYENM 1986.Oxide wear resistant coatings used in industrial application can be prepared by many techniques, J. D.WACHTMAN 2008 made a review on the methods used to prepare ceramic films like TiN , Al_2O_3 and ZrO_2.Spray pyrolysis is attractive because it is a low cost technique K. CHOPRA *et al*. 1983 , therefore ZrO_2 coating is prepared by spray pyrolysis though it is relatively rare G. P. Fotou2000.The aim of this work was to prepare ZrO_2 coating by spray pyrolysis method, and studied some of mechanical properties of coated parts.

EXPERIMENTAL WORK

In this work an aqueous solution of zirconium chloride (ZrCl2) has been used to prepare ZrO_2films. The concentration was (0.1 M). 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 dope ZrO_2 film with elements (Al and Co) at (5wt. %) for each dopant. 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 stainless steel 304 with dimension (1*1*0.5 cm^3) substrates fixed on thermostatic controlled hot plate heater as shows in figure (1). The chemical composition of the 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 ^{o}

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

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

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

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

The microhardness (H.V) was performed with (5g load) by using following equation:

$$H.V=1854.4*p/d^2 \quad (4)$$

Where p is the load and d is the average diameter of the trace. Indenter pin on disk method was used to perform wear testing with 0.5Kg load as in ASTM (G65-91) by using following equation, L. MAISSEL1970:

$$R.W = w_1 - w_2/2\pi*N*R*t \quad (5)$$

Where R.W wear rate, w_1 and w_2 are the sample weight before and after test, N is the number of turn, R is the diameter of the disk length (10 cm) and, t is testing time (minutes).
The corrosion experiments were used to evaluate the efficiency of coatings as protective barriers, by comparing coated and uncoated samples. Weight changes per unit area were calculated. The chemical resistance of the substrates was tested by using different acids (CH_3COOH,H_2SO_4,HCl,HNO_3

RESULTS AND DISCUSSION

Figure (2) shows the variation of microhardness of steel surface with coating by pure and doped ZrO_2 films. It is indicated that there is obvious increasing in microhardness after coating especially after doping with Co. These results are agreed with other researchers [R.Igaku2008, E. Turunen2007].It is important to mention that the microhardness of uncoated steel (304) was 200Kg/mm^2.
Table (2) illustrates the wear characteristics of uncoated and coated steel with pure and doped ZrO_2 films; it can be seen that the wear rate is generally increased with time.But the coating results in an increment in wear resistance especially when coating is dopped with Co. It is found some agreement between present wear results and those obtained by other authors [M. Krzyzak2006, E. Turunen2007].
Since ZrO_2 films are ceramic ones, their hardness and wear resistance are high which are the principle properties of ceramic materials .For this reason the surface microhardness is increased and wear rates are decreased after coating the stainless steel(304).Figures (3,4,5,6,7) show the effect of ZrO_2 coatings on corrosion resistance (weight loss)by immersion the uncoated and coated steel for one hour in heated solutions at 25Cº or 100Cº of (5 wt %) CH_3COOH, H_2SO_4, HCl, HNO_3 and (0.5 Molarity) NaOH respectively. In all conditions , it is illustrated that the mass loss is decreased with coating and ZrO_2 doped with Co has the best corrosion resistance (lowest loss of mass) .By comparing the coated and uncoated surfaces. It is found that the chemical stabilities of the coated surfaces in above solutions at 25Cº are increased by factors 7,10,25,20, and 15 respectively and at 100Cº are increased by factors 6,10,5,14 and 10 respectively. These results have some agreements with other researchers S.Jingyu2006.

Co.To avoid excessive cooling of the substrate, spraying was achieved in periods of about (5 sec) followed by (2 min) wait. Deposition rate was about 2-4nm/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 R.WEAST 1985:

CONCLUSIONS

1-It is possible to obtain ZrO_2 coatings, pure and doped with Al and Co, by spray pyrolysis methods.
2-Microhardness and wear resistance are improved by ZrO_2 coating and the best improvement was obtained by doped coating with Co.
3-Corrosion resistance (weight loss method) is increased with ZrO_2 coatings and the best increment was obvious at coating doped with Co at different solution.
4-As temperature is increased the corrosion resistance of coated and uncoated surfaces are decreased.
5-The best corrosion resistance improvement was in HCl.

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) at(5wt%)and NaOH at(0.5 Molarity),at temperature 25 C° and 100C°.SEM examinations of the coats are shown in other research published by the authors[Ali H. Ataiwi and Alaa A. Abdul-Hamead].

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Table (1) Chemical composition of steel 304

Element	304(Austenitic) Standard wt%	304(Austenitic)Measured wt%
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

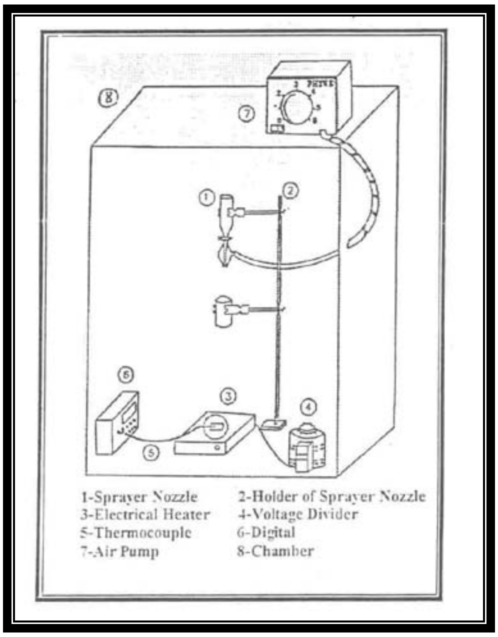


Figure (1) Diagram of the spraying apparatus.

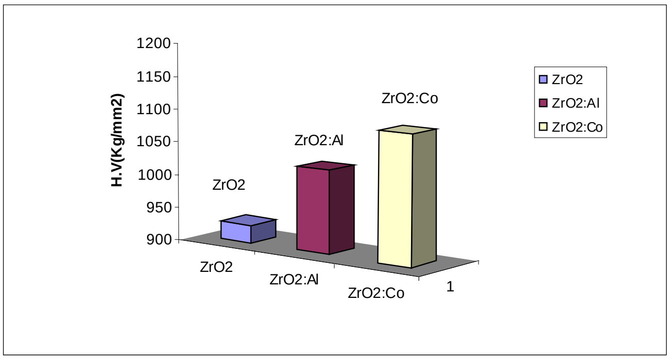
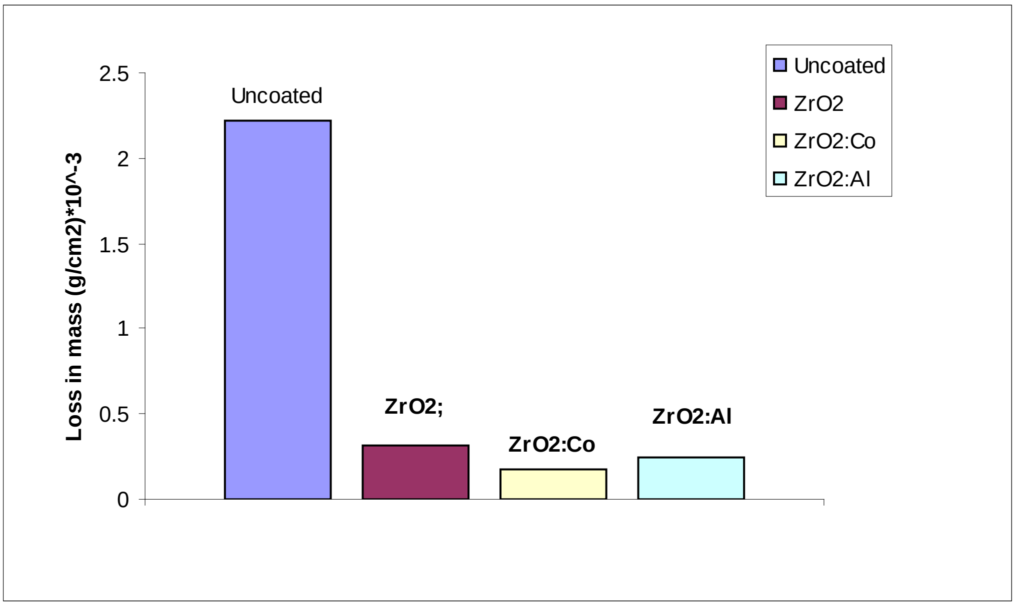


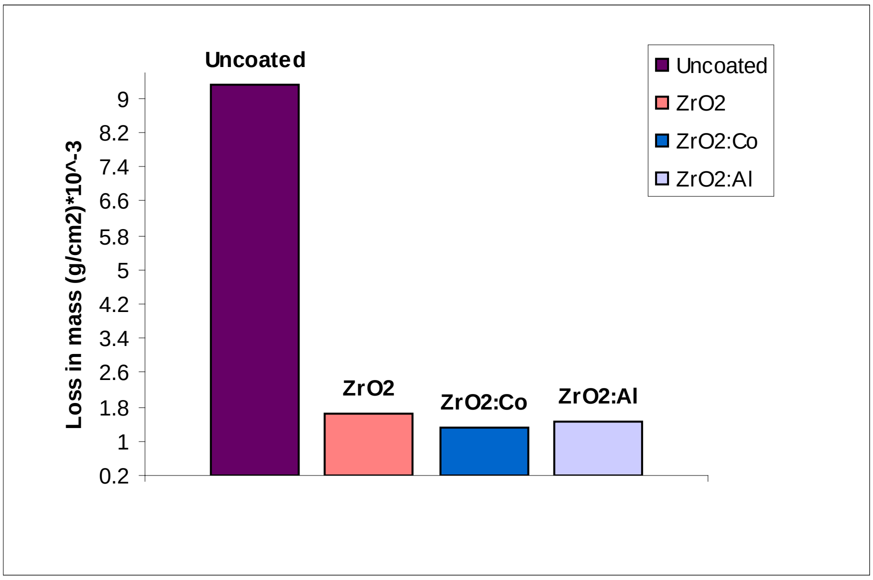
Figure (2) Microhardness of pure and doped ZrO2films.

Table (2) Variation of wear rate of un coated and after coated with ZrO_2 (pure and doped) steel with time.

Time(min)	Wear rate(gm/cm)			
	un coated steel	Coated with		
		ZrO_2	ZrO_2: Al	ZrO_2: Co
10	7.5*10^-7	10^{-10}*10	7.5^{-10}*10	3.79^{-10}*10
20	11.3*10^-7	11.3^{-10}*10	7.5^{-10}*10	3.79^{-10}*10
30	12.6*10^-7	12.6^{-10}*10	8.8^{-10}*10	5.05^{-10}*10
60	10.11*10^-7	13.2^{-10}*10	9.4^{-10}*10	5.68^{-10}*10

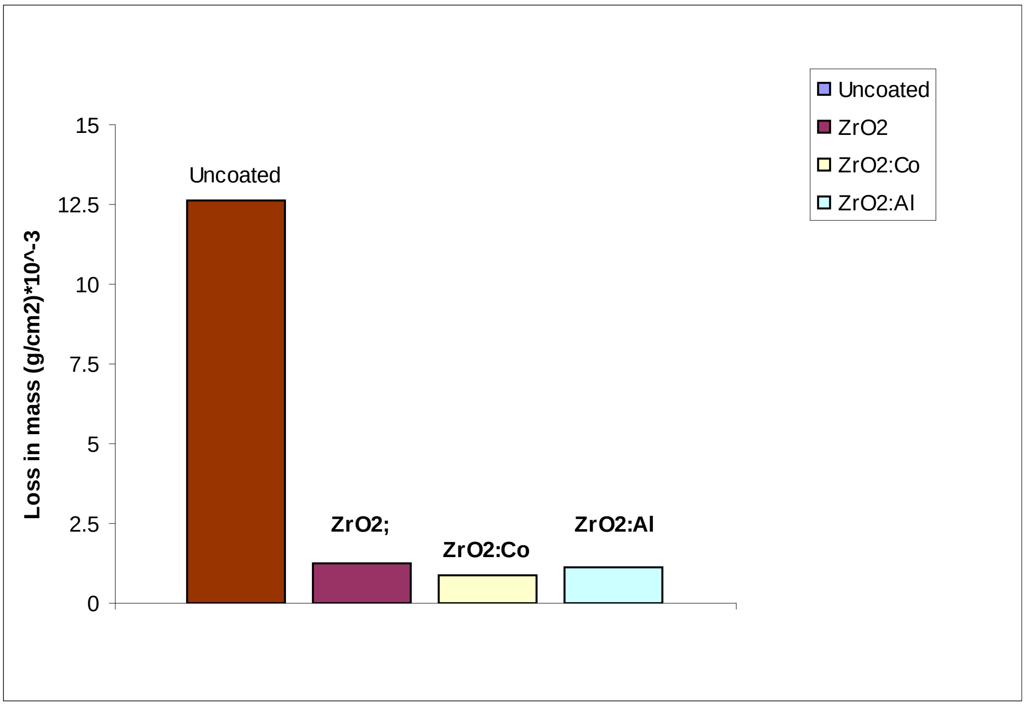


(a)at 25C⁰

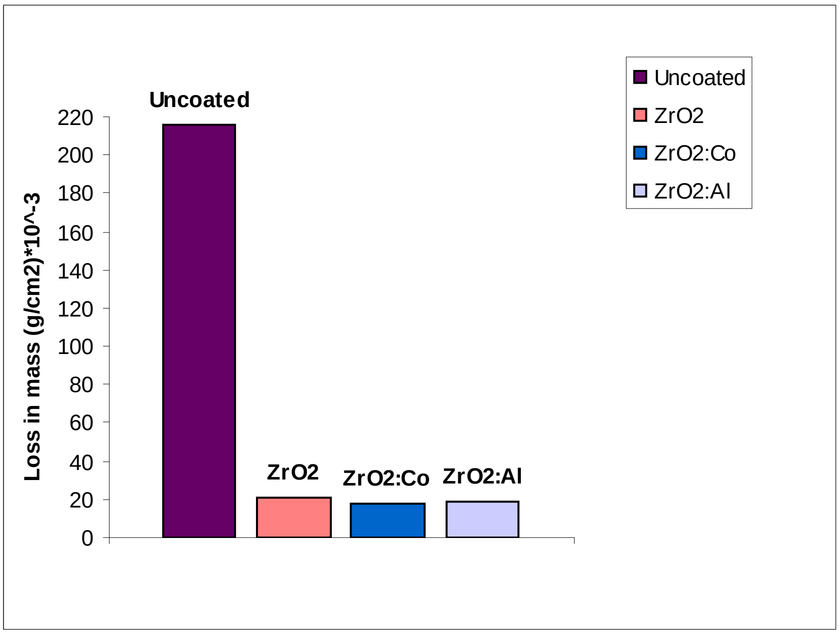


(b)at 100 C⁰

Figure(3) Weight loss for uncoated and coated steel by pure and doped ZrO_2 in (5wt%) CH_3COOH acid for 1 hour (a) 25 C⁰, (b)100C⁰.

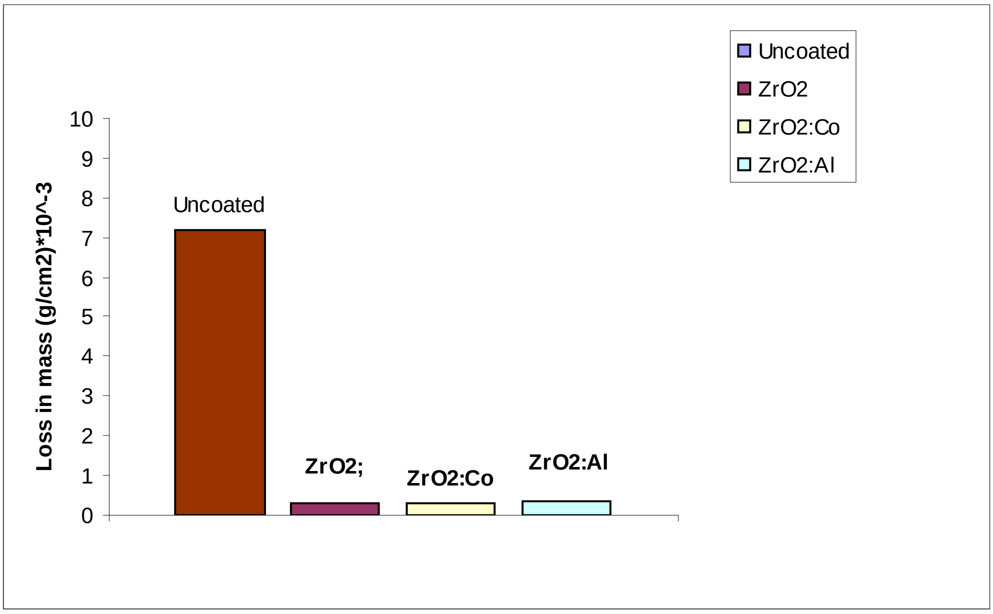


(a)at 25C^0

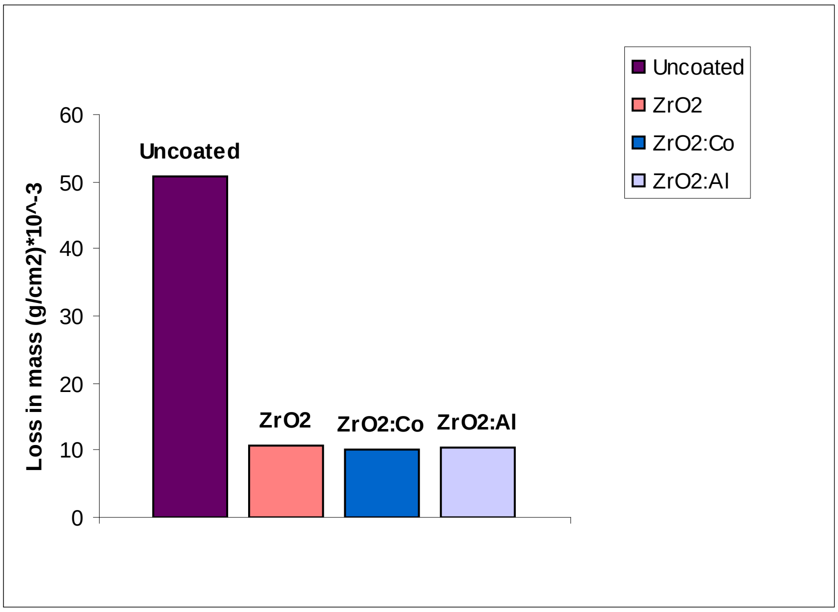


(b)at 100 C^0

Figure(4) Weight loss for uncoated and coated steel by pure and doped ZrO_2in (5wt%) H_2SO_4 acid for 1 hour (a) 25 C^0, (b)100C^0.

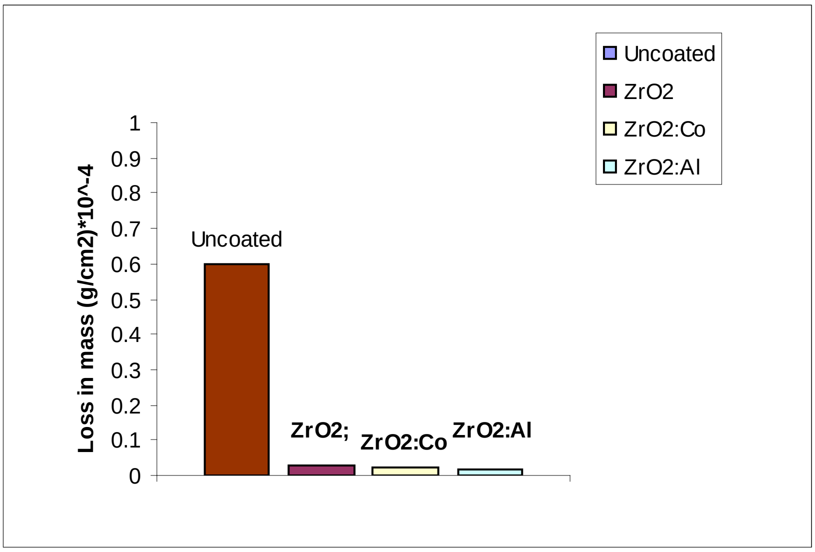


(a)at 25C⁰

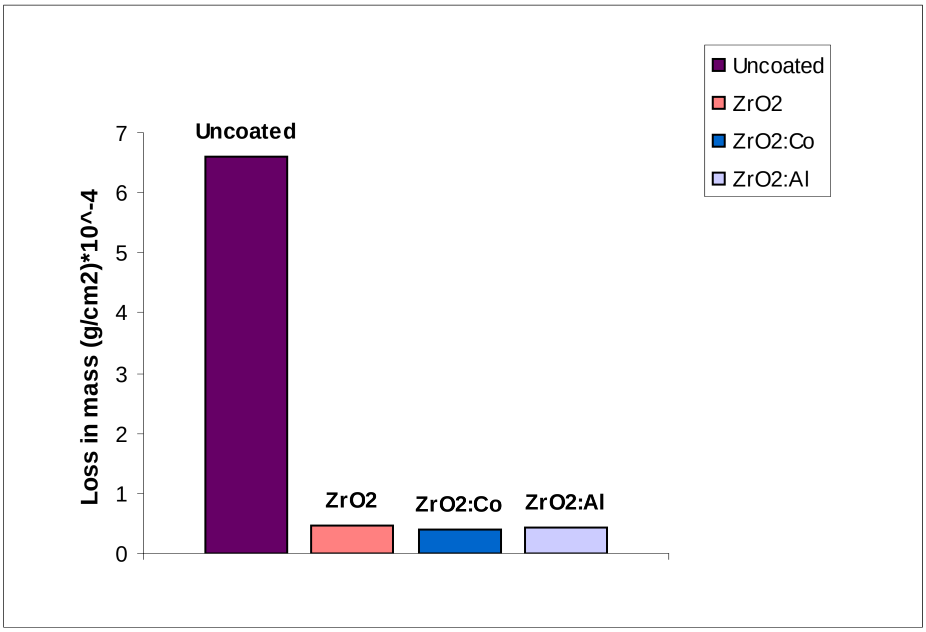


(b)at 100 C⁰

Figure(5) Weight loss for uncoated and coated steel by pure and doped ZrO_2 in (5wt%) HCl acid for 1 hour (a) 25 C⁰, (b)100C⁰.

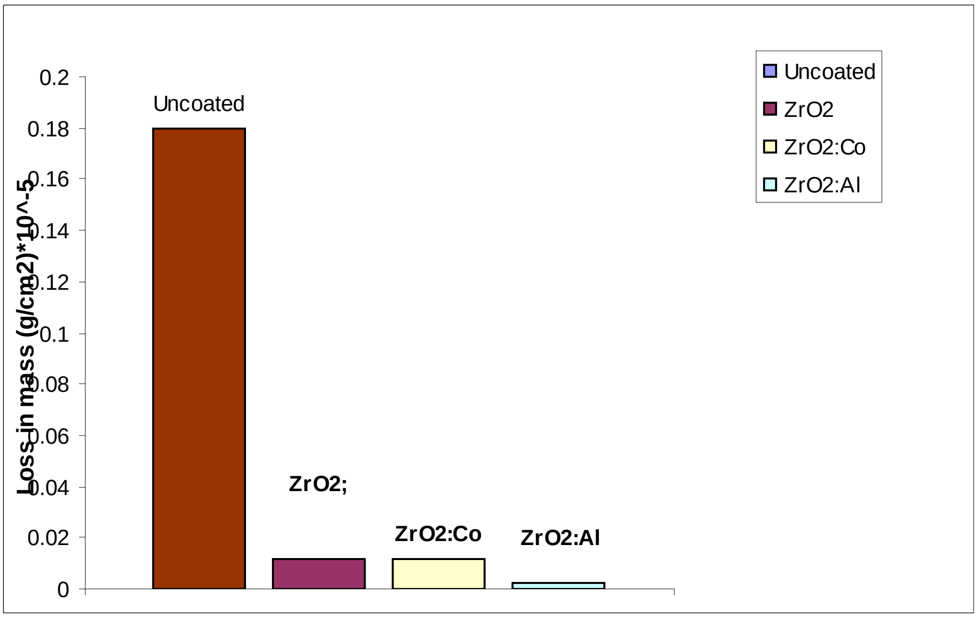


(a)at 25C⁰

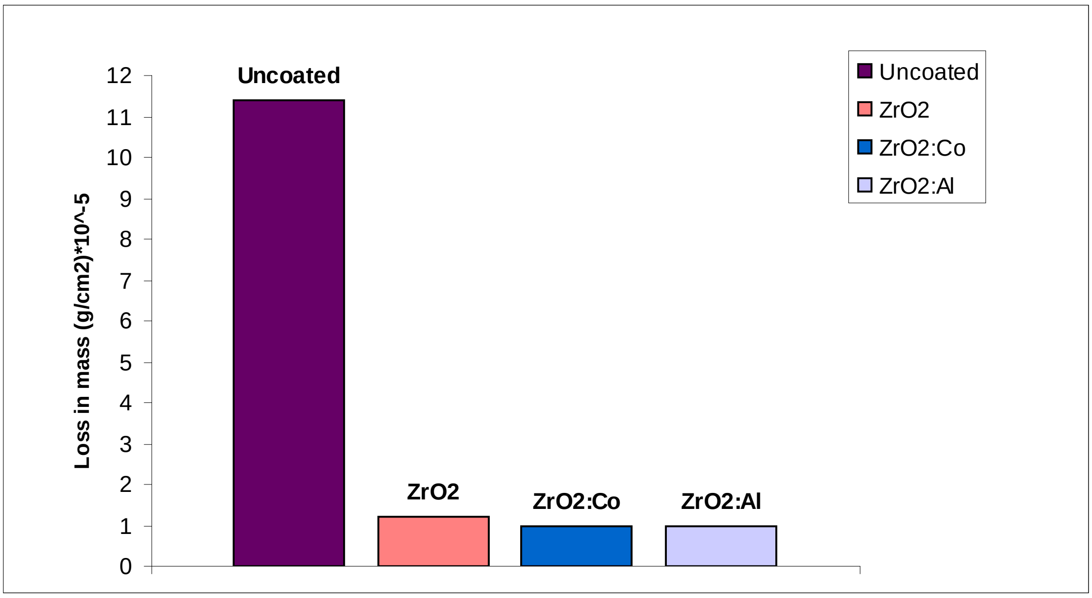


(b)at 100 C^0

Figure(6) Weight loss for uncoated and coated steel by pure and doped ZrO_2 in (5wt%) HNO_3 acid for 1 hour (a) 25 C^0, (b)100C^0.



(a)at 25C⁰



(b)at 100 C⁰

Figure(7) Weight loss for uncoated and coated steel by pure and doped ZrO_2in (0.5Molarity) NaOH acid for 1 hour (a) 25 C^0, (b)$100C^0$.