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A STUDY FOR SOME OF MECHANICAL PROPERTIES OF AL_2O_3 CERAMIC THIN FILM PREPARED BY SPRAY PYROLYSIS METHOD

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ABSTRACT

In the present work Al_2O_3 thin film has been deposited on glass and stainless steel 304 substrate by spray pyrolysis technique. Al_2O_3 was deposited with different three element(Al, Fe ,Cu) for five different percentages(1,2,3,4,5 wt %), the film was test by XRD measurements , and the topography of the films has been tested by using optical microscope, also measuring open porosity ,and Apparent density was calculated. Some of mechanical characteristics have been studied (microhardness, wear resistance). The results of XRD show that the film was crystalline with α- Al_2O_3 phase and grain size was 60 nm and stress ratio was 0.027%. Apparent density was 2 g/cm^3 for pure Al_2O_3 film to 3.1g/cm^3 for 5 wt% of Fe ,and open porosity was 2pore/cm^2.The testes were proved that the mechanical properties results were improved after doping specially with Fe. The microhardness of the films has been improved after doping from 1346.9 Kg/mm^2 for pure Al_2O_3 film to 1648.3 Kg/mm^2 for 5 wt% of Fe on glass, and from 1413.1 Kg/mm^2 to 1947.5 Kg/mm^2 on stainless steel 304.Also wear resistant has been improved for the films that deposited after doping from $5.68*10^{-9}$ g/cm^2 for pure Al_2O_3 to 3.03 $*10^{-9}$ g/cm^2 for 5 wt% of Fe.

Key word: spray pyrolysis, *Al_2O_3 film*, microhardness, wear resistant, ceramic film.

دراسة بعض الخواص الميكانيكية لاغشية

Al_2O_3السيراميكية المحضرة بطريقة الرش الكيماوي الحراري

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الخلاصة

في هذا البحث تم ترسيب أغشية من الالومينا Al_2O_3 على قواعد من الزجاج والفولاذ المقاوم للصدا 304 وتمت إضافة ثلاثة أنواع من المعادن وهي الحديد و النيكل و النحاس و بخمس نسب وزنيه مختلفة 1,2,3,4,5 wt% الى الالومينا و بطريقة الرش الكيماوي الحراري.تم اولا تحليل الاغشية بأستخدام حيود الأشعة السينية XRD و فحص البنية المجهرية باستخدام المجهر الضوئي وكذلك قياس المسامية المفتوحة و حساب الكثافة الظاهرية،و ايظا تم دراسة الخواص الميكانيكية (الصلادة الدقيقة و مقاومة البلى) . بينت نتائج XRD ان الاغشية المترسبة كانت متبلورة والطور المتكون هو α- Al_2O_3 و الحجم الحبيبي بلغ 60 nm ونسبة الاجهادات الداخلية 0.027% . بلغت قيمة الكثافة الظاهرية للاغشية النقية 2 g/cm^3 أعلى قيمة للأغشية المشابه 5 wt% of Fe هي 3.1g/cm3 قيمة المسامية بلغت 2 Pore/cm^2 بصورة عامة.أثبتت الفحوصات تحسنا ملحوظا في الخواص الميكانيكية بعد الاشابة و خاصة الاغشية المشابة بالحديد ،حيث ازدادت الصلادة الدقيقة من 1346.9 Kg/mm^2 للاغشية النقية الى 1648.3 Kg/mm^2 لـ 5 wt% of Fe في غشاء Fe: Al_2O_3 أما بالنسبة إلى الأغشية المرسبة على الزجاج من 1413.1 Kg/mm^2 للاغشية النقية إلى 1947.5 Kg/mm^2 للاغشية المشابة بالحديدو بنسبة 5 wt% of Fe .أما مقاومة البلى فقد تحسنت بشكل كبير بعد ترسيب الالومينا على الزجاج و الفولاذ المقاوم للصدا 304 من $5.68*10^{-9}$ g/cm^2 الى 3.03 $*10^{-9}$ g/cm^2 لاغشية 5 wt% of Fe

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INTRODUCTION

Thin oxide film have found application in many areas ranging from electronic circuits to wear and corrosion protection like cutting tool ,D.NGUYENM(1986)study amorphous Al_2O_3 and Al_2O_3-ZrO_2 films prepared by spray pyrolysis with XRD and SEM, and FREDERICK J.(2006) prepared Al_2O_3 films by PVD and CVD technique and he found that the thickness was (1-10 µm) and grain size was(100 nm).Alumina 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., Internet S.L (2008), K. CHOPRA, S. (1983). Oxide wear resistant coatings used in industrial application can be prepared by many techniques JOHN D. (2008), he made a review on the methods used to prepare ceramic films like TiN ,TiC and Al_2O_3. BJORN L.(2001) used mainly CVD, PVD technology to prepare Al_2O_3 and studded five different types of wear for TiN, Al_2O_3 and TiAlN .Spray pyrolysis is attractive because it is a low cost technique references to thin coatings of Al_2O_3deposited by spray pyrolysis, have been relatively rare D.Nguyen (1984), L. MAISSEL (1970). The aim of this work is to produce a thin ceramic film from Al_2O_3 by spray pyrolysis method and doping the films with some elements then study some of their mechanical properties.

EXPERIMENTAL WORK

In this work an aqueous solution of Aluminum nitrate [$Al(NO_3)_2.9H_2O$] has been used in this study to prepare Al_2O_3films. The concentrations was used (0.3 M). The acidity was maintained to be 3-4 pH during spraying .Three salts [$2Fe(NO_3)_2.9H_2O$, $NiCl_2$, and $CuCl_2$) were used to dope Al_2O_3film with three elements (Fe , Ni and Cu) respectively at(1,2,3,4 and 5wt.%) for each dopant. The choice of these dopants is done to cover group (VII) and transition elements of the periodic table. The deposition of the films is made by spray pyrolysis technique. The spraying apparatus used in this study was manufactured locally in the university laboratories with inexpensive equipment. In this technique, the previously prepared aqueous solutions were atomized by a special nozzle glass sprayer at heated glass and stainless steel 304 substrates fixed on thermostatic controlled hot plate heater, the chemical composition is listed in table 1. Air was used as a carrier gas and to atomize the spray with the help of an air blower. The substrate temperature was maintained to be 450 °C during spraying with ±10 ^oC. To avoid excessive cooling of the substrate, spraying was achieved in periods of about 5 s followed by 2 min wait. Deposition rate was about 2-4 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 (28±1 cm.) The spray of the aqueous solution yields the following chemical reaction R.WEAST (1985):

$$2Al(NO_3)_3.9H_2O \xrightarrow{450\ C} Al_2O_3 \downarrow + 6NO_2 \uparrow + 9H_2\uparrow \quad (1)$$

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

$$2Fe(NO_3)_2.9H_2O \xrightarrow{450C} 2\ Fe \downarrow + 6NO_2 \uparrow + 9H_2O\uparrow \quad (2)$$

$$NiCl_2 \xrightarrow{450C} Ni \downarrow + Cl_2\uparrow \quad (3)$$

$$CuCl_2 \xrightarrow{450C} Cu \downarrow + Cl_2\uparrow \quad (4)$$

Thickness of Al_2O_3 was 1µm, to determine the nature of the growth and the structural characteristics of Al_2O_3 films. 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 (46-1212) card. The topography of the Al_2O_3 surface was inspected with optical reflected-microscope type (Nicon 73346) under magnification of X 108. The vicker's microhardness was performed with (5g load) by using the following reaction:

H.v =1854.4p/d2 (5)

Where p is the load and d is the average diameter of the trace.
Wear test was done by using pin on disk method with 0.5Kg load as in ASTM (G65-91) by using following reaction:

R.W = (m1-m2)/2π*V*S*t (6)

Where m1 is the sample mass before test and m2 is the mass after test ,V is the velocity of the disk, S is the diameter of the length and t is test time(minuet), apparent density was calculated from films mass and volume ,open pores was measured by used prop point method, Internet RES 2008.

RESULTS AND DISCUSSION

Figure 1 shows the XRD chart of the Al_2O_3 film ,and observed that the films was crystalline Al_2O_3 with α- Phase agree with ASTM cart (46-1212) the grain size was (60 nm) for pure Al_2O_3 and (2θ=35.19) as listed in table 2. FREDERICK find grain size was 100 nm for Al_2O_3 film prepared by PVD. Figure 2 illustrates the topography of pure Al_2O_3 film were the surface is white and little mite with some pit on surface of the film as show in Figure 2-1. In Figure 2-2 illustrates the type of circles that happen in the surface of the films because of the drupe that fill on the surface and this result is agree with lettrucare CHOPRA, MAISSEL. Figure 2-3 shows the interface between area coated with Al_2O_3 and beside area which does not coated, some times a little crack can be happen because of heat change in the lattice during spray time. The topography of doped Al_2O_3 films shows in figures below, the surfaces were also white and little mite without any colors (another metal oxides) agree with MITCHELL C.(1998). Figure 2-5 shows Al_2O_3:Fe films in a: (1wt%) doping of iron and in b(3wt%) and in c: (5%wt) assume in the Figure. In Figure 2-6 shows Al_2O_3 : Ni films at a :(1wt%) of Ni and in b:(3wt%) and in c: (5wt%) .While in figure 2-7 shows Al_2O_3 : Cu and in a: (1wt%) of cu , b: (3wt%) and in c: (5wt%). Figure 2-8 shows the Al_2O_3 film deposited on stainless steel 304 a- pure Al_2O_3 ,b- AL_2O_3:Fe(1wt%) films on steel substrate, in- c AL_2O_3:Ni(1wt%) films on stainless steel substrate, in -d AL_2O_3:Cu (1wt%)films on steel substrate H.K(2005). Figure 3 show apparent density which is change with doping percentage while open porosity in figure 4 show little effected with doping change. Figure 5 show the vicars microhardness of the films on glass the H.V because of doping percentage in areas in Fe doping the effect is more than Cu, in figure 6 show the vicker's microhardness of the films on steel304 which is more than in glass because of structure effect of the film on stainless steel 304K Christova (1991), D.F(1999).Figure 7 show the wear of stainless steel 304 and in Figure 8 the films wear on stainless steel 304.Rate of wear change with doping percentage of the metals Internet DOI (2005).

CONCULUSION

The main conclusion of this research are:

1-Al_2O_3 films was prepared by spray pyrolysis technique.
2-Chosing the right deposition distains and temperature help by reducing the internal stress ratio.
3- No oxides has been deposited with Al_2O_3 films, and this give use perfect percentage of doping.
4-Increasing thin films density after doping.
5-Redusing open porosity after doping.
6-Increasing microhardness and reducing wear rate resistance after doping.

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List of symbol

Symbols	Description
A.D	Apparent density

ASTM	**A**merican **S**tandard for **T**esting **M**aterials
g.s	Average grain size
hkl	Miller indices
H.v	Microhardness of vicker's
I_m	Measured intensity
I_{ASTM}	ASTM standard intensity
M	Molary
R.W	Rate of wear
XRD	X-ray diffraction
(δ)	Internal strains

Table 1 Chemical composition of stainless steel 304.

Element	**Austenitic stainless steel -304**
Carbon	0.08
Manganese	2.00
Phosphorus	0.045
Sulfur	0.03
Silicon	1.00
Chromium	18.00-20.00
Nickel	8.00-10.50
Iron	Balance

Table 2 Result of XRD of Al_2O_3 film.

$2\theta_{ASTM}$	$2\theta_{M}$	hkl	$Int._{ASTM}$	$Int._{M}$	δ	g.s
35.182	**35.19**	**104**	**100**	**91.19**	**0.027%**	**60nm**

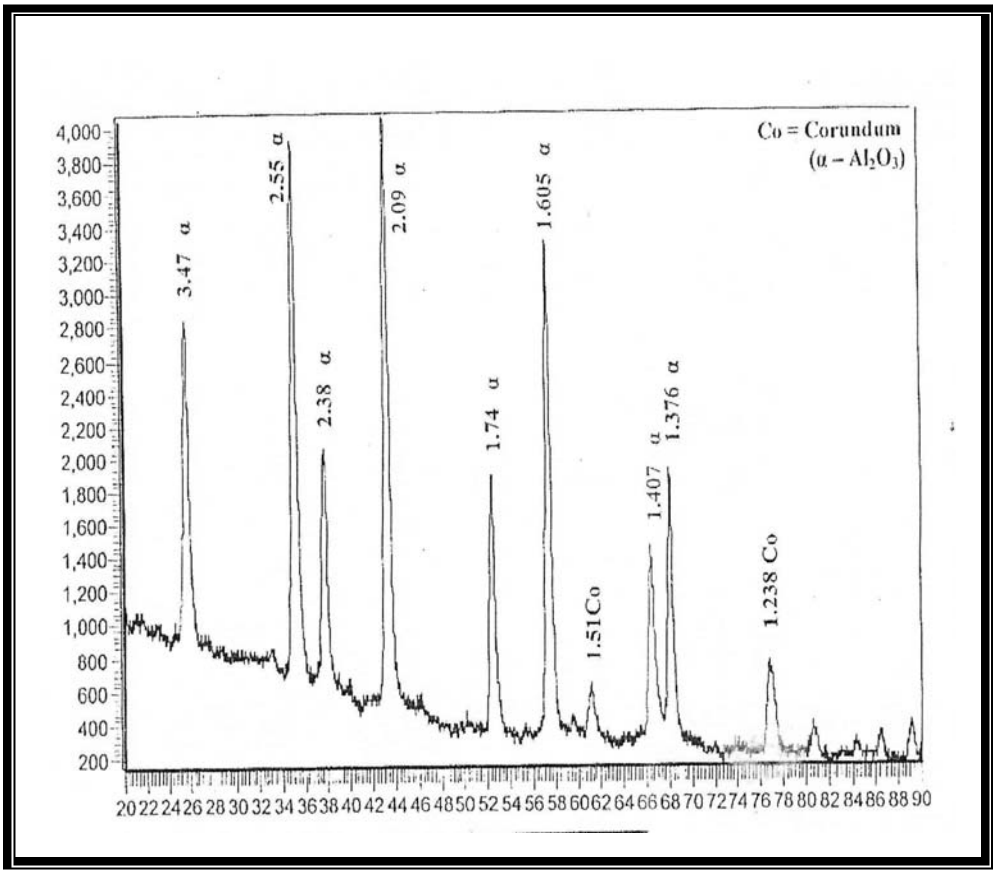


Figure 1 XRD of Al_2O_3 film.

Figure 2-2 Circle type of deposited Al_2O_3 film on glass substrate.

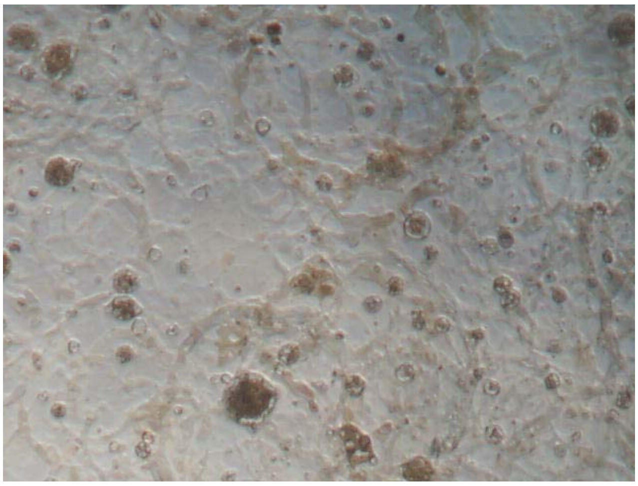
Figure 2-1 Pure Al_2O_3 film on glass substrate.

Figure 2-4 Some crake in Al_2O_3 film on glass substrate.

Figure 2-3 Interface of Al_2O_3 film on glass substrate

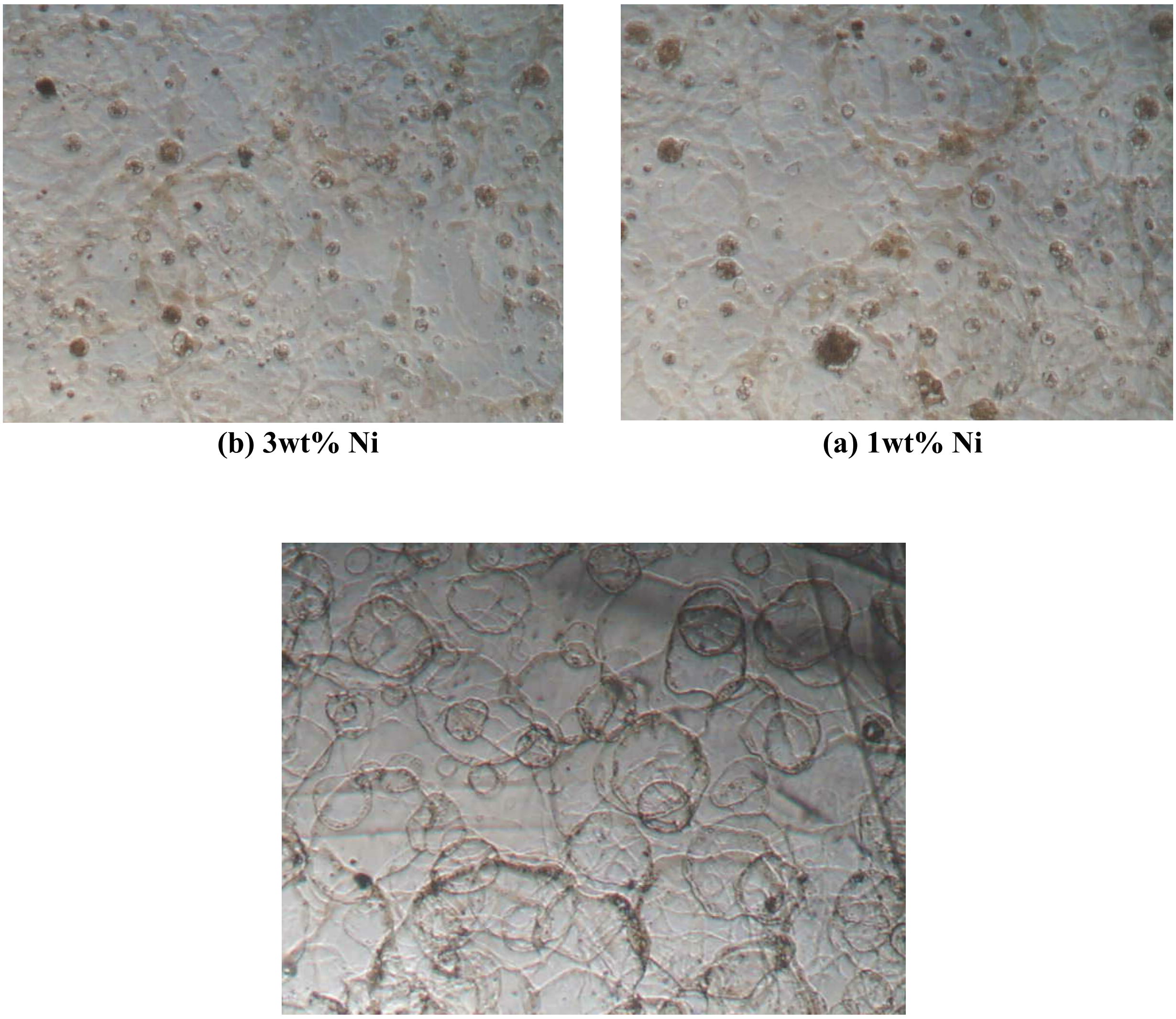
(a) 1 wt% Fe

(b) 3 wt% Fe



(c) 5 wt% Fe

Figure 2-5 Al_2O_3:Fe film on glass substrate.

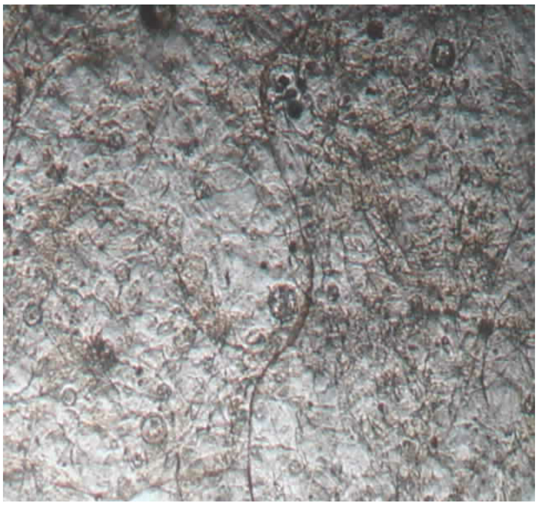


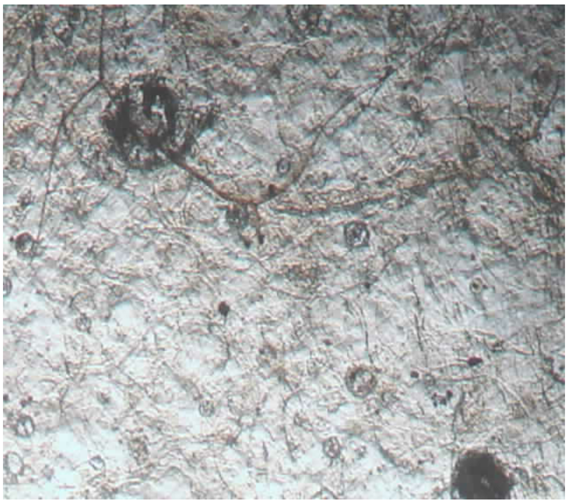
(b) 3wt% Ni

(a) 1wt% Ni

(c) 5wt%Ni

Figure 2-6 Al_2O_3:Ni films on glass substrate.



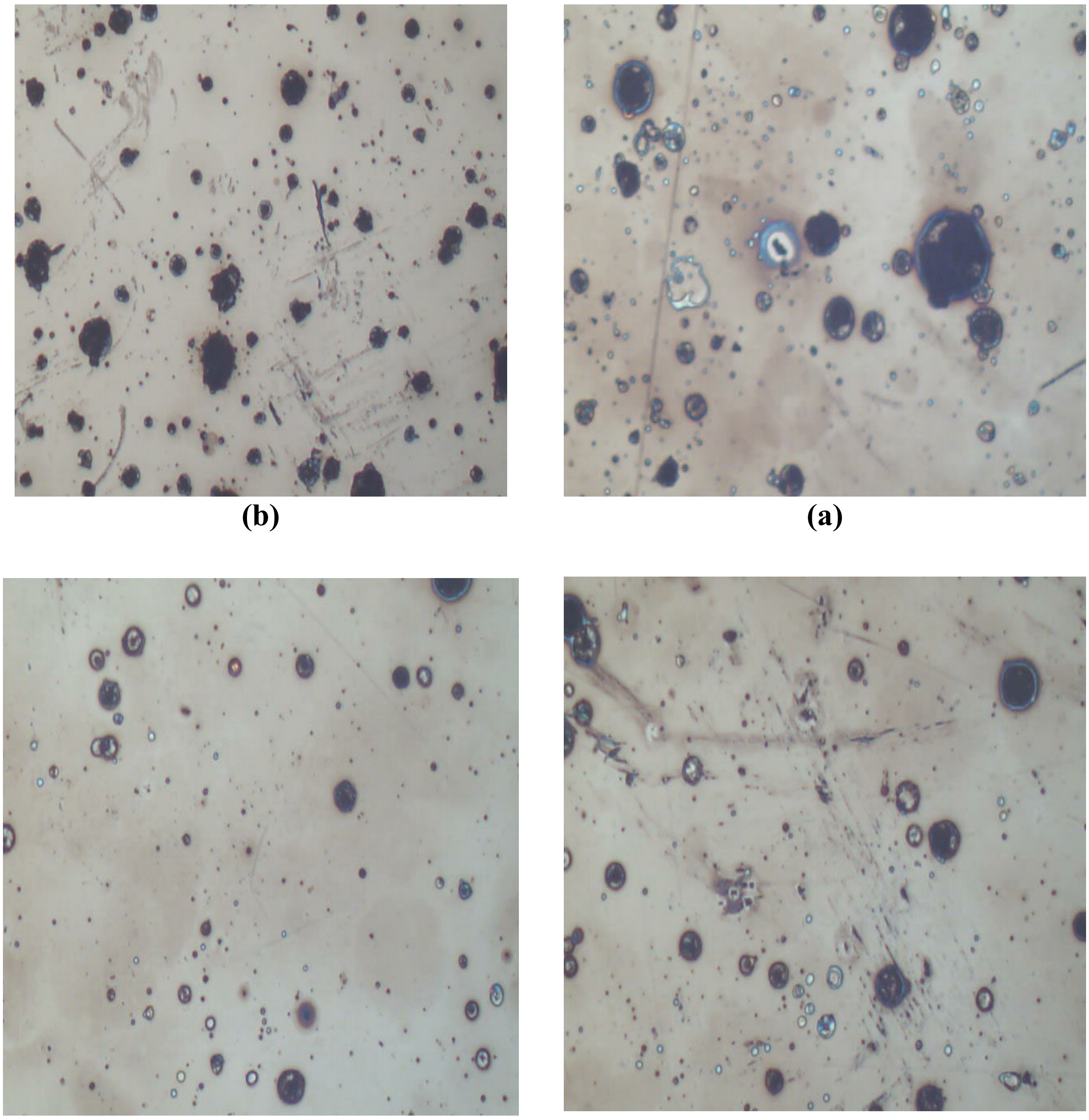


(b)3wt%Cu

(a) 1wt%Cu

(c) 5wt%Cu

Figure 2-7 Al_2O_3:Cu films on glass substrate.



(b) (a)

(d) (c)

Figure 2-8 (a) Al_2O_3 films on stainless steel-304 substrate (b) Al_2O_3:Fe(1wt%) (c) Al_2O_3: Ni(1wt%) (d) Al_2O_3:Cu (1wt%).

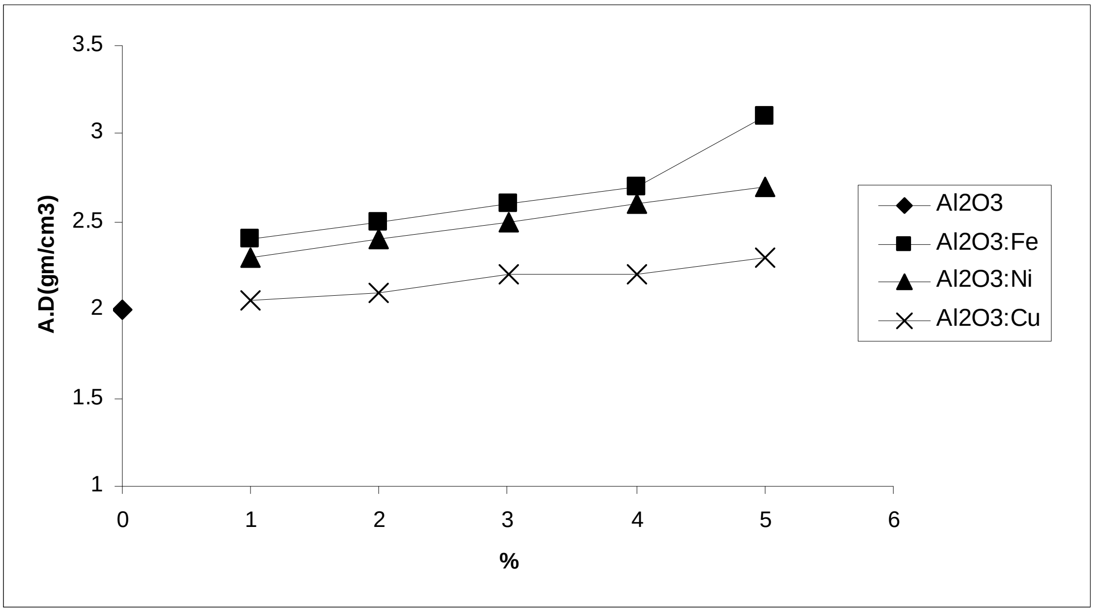


Figure 3 Apparent density of Al_2O_3 film.

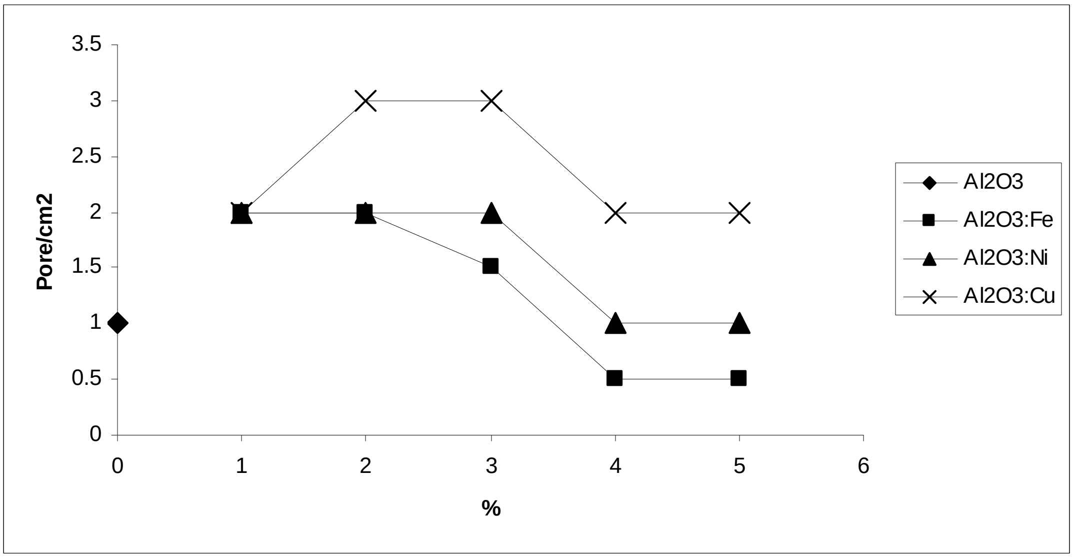


Figure 4 Open pores in Al_2O_3 film on stainless steel-304.

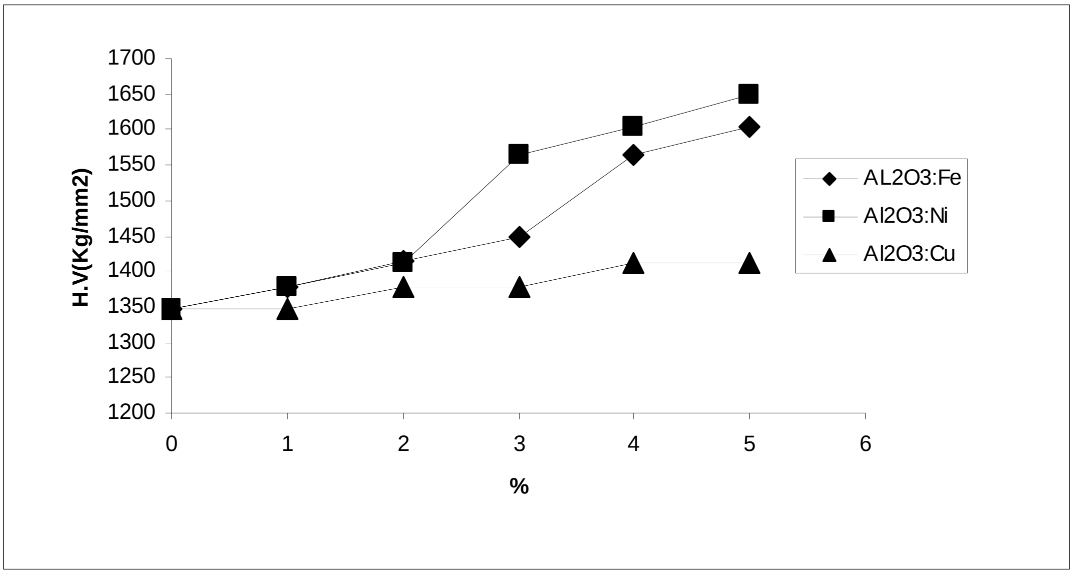


Figure 5 Microhardness of vicker's Al_2O_3 films on glass.

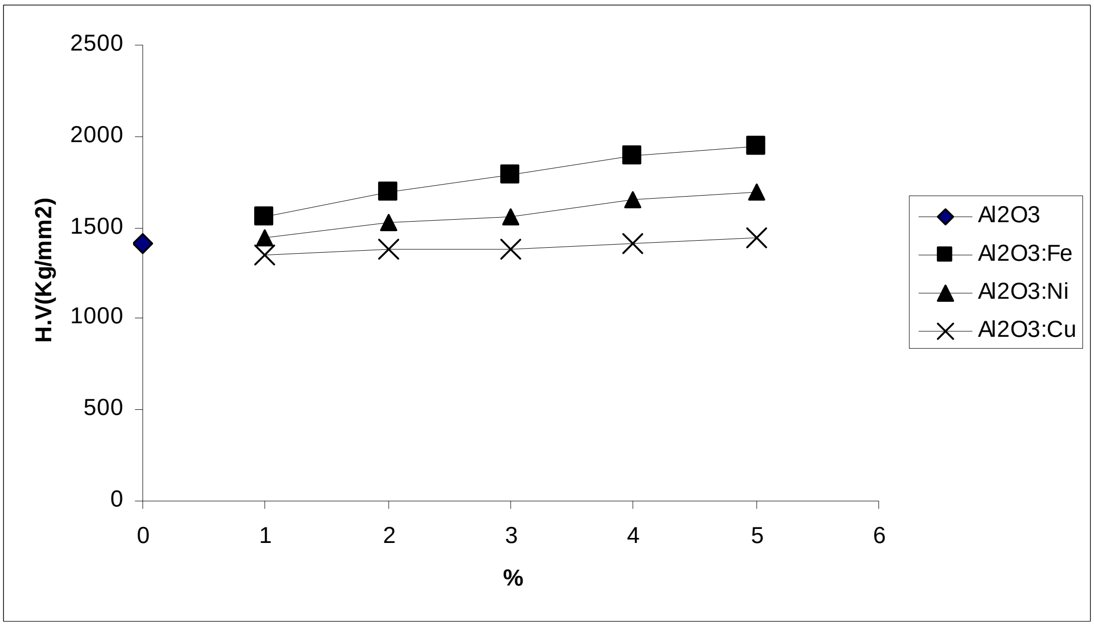


Figure 6 Microhardness of vicker's Al_2O_3 films on stainless steel-304.

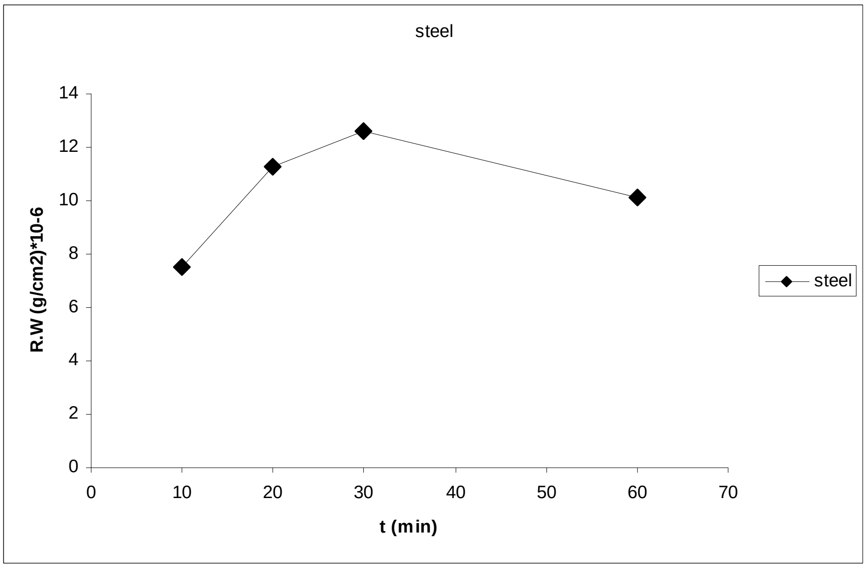


Figure 7 Wear result of stainless steel-304.

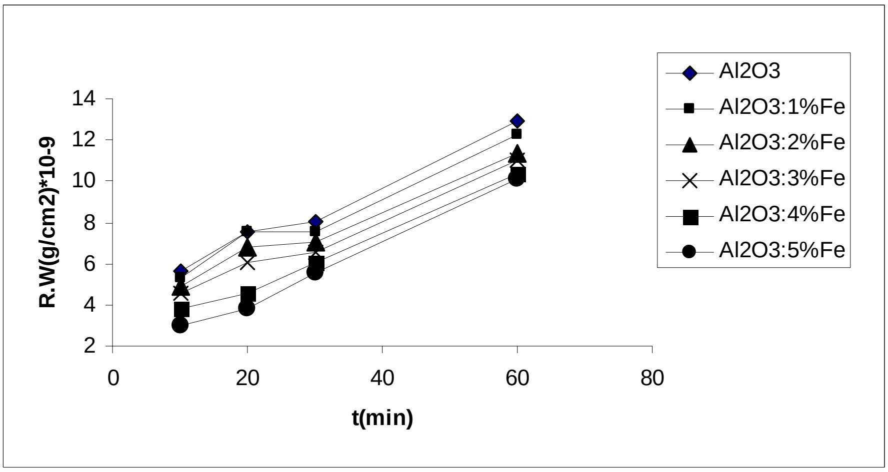


Figure 8 Wear result of Al_2O_3:Fe films.

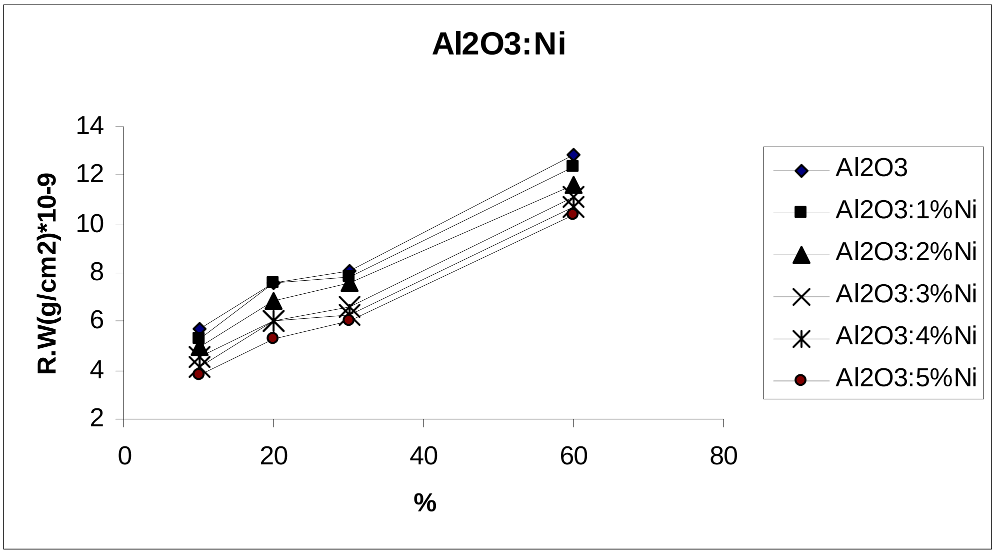


Figure 9 Wear result of Al_2O_3:Ni films.

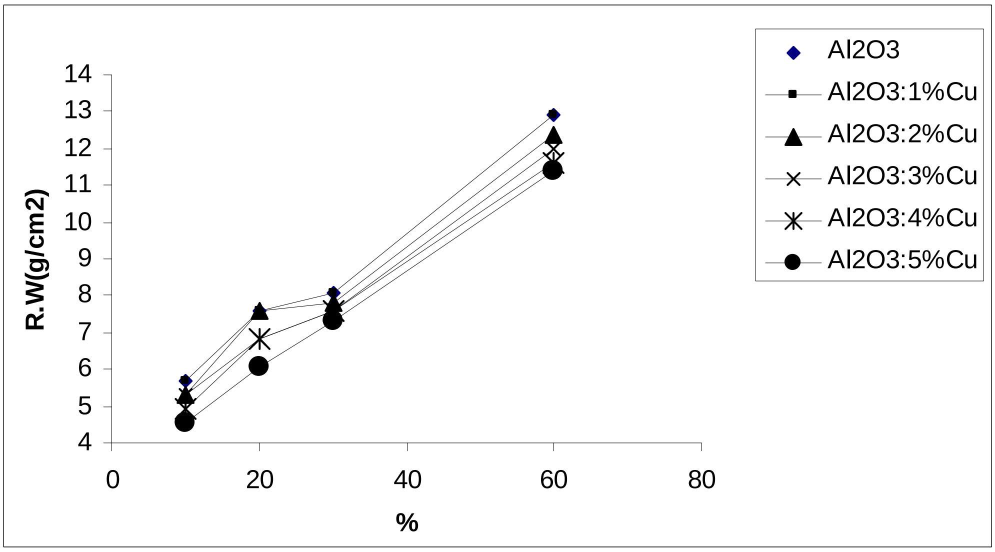


Figure 10 Wear result of Al_2O_3:Cu films.