Study the Effect of Co Concentration in Nico Thin Films on Some Structure and Mechanical Properties

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Abstract

Electroplating process has been used to prepare Magnetic NiCo alloys thin film with thickness of 1µm on brass alloy substrate using different Co concentrations .Surface morphology, XRD, atomic absorption, apparent density, open porosity, stresses and microhardness of pure and alloys thin film has been investigated. Results indicated that the pure and alloy of thin films was polycrstaline with (111) domain orientation changed to (101) with increment Co deposited percentage, which is spontaneously increase with Co molarity increased in the deposition solution.Microstructure for thin films change from nodular structure to pyramidal and dendritic structure with changing Co content in film. Apparent density for prepared thin films was less than theoretical density about ($8g/cm^3$), and varying with actual Co deposited content. Open porosity also reduced in general with increment of Co content. Mechanical properties shows alteration in internal stress behavior of deposited thin films from compressive stress to tensile stress at (0.05M) of Co. Microhadness also increased with increasing in the Co percentage in deposited thin films,to about($467Kg/mm^2$).

Keywords: electroplating, alloy plating, microhardness, internal stress, thin film.

دراسة تاثير تركيزCo في أغشيةرقيقة من NiCo على بعض الخواص التركيبية و الميكانيكية

الخلاصة

استخدمت طريقة الترسيب الكهربائي لتحضير اغشية سبائكية مـــنNiCo مغناطيســـية و بسمك 1µm وبنسب مختلفة من Co على قواعد لسبيكة من البراص .تـــم فحـــص التصـــوير المجهري و حيود الاشعة السينية و التحليل الكيمياوي و الكثافة الظاهرية و المسامية المفتوحة و الاجهادات الداخلية و الصلادة الدقيقة للاغشية المرسبة النقية و السبائكية .بينت النتـــائج بـــأن الاغشية المترسبة النقية و السبائكية متعددة التبلور و بالاتجاهية (111) ويتحول الى (101) مع زيادة نسبة الكوبلت المترسبة و التي تزداد تلقائيا مع زيادة المولارية المضـــافة الـــى محلـــول الترسيب. وتغيرشكل البنية الدقيقة لسطح الغشاء الرقيق من عقدية ناعمة الى شجيرية وهرمية تقريبا مع تغير نسبة الكوبلت بالغشاء.وكانت الكثافة العملية للاغشية المحضرة اقل من الكثافة النظرية حوالي ($8g/cm^3$) وتغيرت مع تغير نسبة الكوبلت المترسبة فعليا .ايضا انخفضت المسامية المفتوحة على العموم مع زيادة نسبة الكوبلت.الخواص الميكانيكية للاغشة بينت تغير في سلوك الاجهادات الداخلية في الاغشية الرقيقة المترسبة من ضغطية الى شدية عنـــد (0.05M of Co)

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,كذلك ازدادت قيمة الصلادة الدقيقة لهذه الاغشية مع زيادة نسبة الكوبلت بالاغشية الرقيقة المرسبة,وصلت الى حوالي($467Kg/mm^2$).

1. Introduction

Electrodeposited iron group thin films Fe, Co and Ni have been carried out because of potential applications in computer read/write heads[1,2], microelectromechanical systems (MEMS)[3-5]ultralarge scale integration (ULSI) devices [6,7] and Magnetic.
Nanowires[8].Electrochemical processes (electrodeposition and electroless deposition) have many advantages over vacuum processes because of room temperature operation, various deposition parameters, easy scale up and maintenance, low production cost, relatively rapid deposition rate, the capability of handling complex geometries, and the ability to ‘‘tailor’’ deposit structure and properties. Electrodeposition deposits are Magnetic materials have recently been incorporated into MEMS devices such as sensors, microactuators, micromotors, and frictionless microgears because electromagnetic-actuated MEMS are more durable for force applications in severe environments compared to electrostatic-actuated MEMS[9,10] . To incorporate magnetic materials into MEMS devices, magnetic thin films must have good adhesion, low-stress, good corrosion resistance, and be thermally stable with excellent magnetic properties[11]. Magnetic layer thicknesses in MEMS can change from a few tenths to hundreds of micrometers up on the applications. In particular, stress of the deposited films play important role in incorporation of magnetic materials into MEMS devices. High stress in magnetic thin/thick films may result in neglecting of MEMS devices[12,13], because of deformation or detachment of the deposited films from the substrate like Si substrate. Although numerous studies have been carried out to investigate binary and ternary iron group magnetic thin films, there is a lack of systematic studies about the stress issue. Various from binary CoFe and CoNi ,ternary CoFeB, CoFeCr, CoFeP,CoFeCu, CoNiFe and quaternary alloys like CoNiFeS, CoFeNiCr, CoFeSnP, and CoNiFeB alloys[14].The aim of this work is to prepare NiCo thin films alloy from chloride baths and study some of their structure and mechanical properties .

2. Experimental Procedure:-

Copper alloy substrates have been used with (40*2*0.1) mm dimensions, its chemical composition shown in Table (1). At first we cleaned up the substrate by using Alkaline cleaning bath ,then washed by distilled water, after that surface will be activated by picking to remove the oxidation by using HCl acid (30%) diluted in (10%) at 40°Cfor 10sec then drying sample in air, figure (1-a)shows the samples(substrates) before and after depositing. Electroplating solutions was prepared as shown in Table (2) [15], and figure (1-b) shows electrodeposition unit. Reflected metallurgical microscope type (XJL-101) was used to test the films surface with (X200), the NiCo alloys thin films was also characterized by x-ray diffraction using Philips diffractometer with target of Cu-kα_1 with wave length of (λ = 1.54056 Å

), the scanning speed was 3%. The data was compared with that of ASTM card. The chemical analysis of NiCo alloys thin film was done also after dissolved it ,NiCo thin film thickness t was calculated by using depth of focusing method by using following relation below, and it was 1µm[11]:

$t=(m1-m2)*N$ …….(1)

Where m1, m2 is the reading in microscope at two adjacent sides coated and uncoated with NiCo thin film and N is the lens factor. Apparent density (ρ) was calculated by using the relation [11]:

$\rho=\Delta m/t*A$ …….. (2)

Where Δm is the film mass(g), A the area of Cu alloy substrate (cm^2).Open pores were done by prop point method ASTM (D3258-04) [16], where open pores calculated from the relation:

$P=N_p/A_t$ ……. (3)

P :porosity (p/cm^2)N_p number of pores, A_t test area (cm^2).

Internal stresses were calculated by using beam bending method and as the following relation and after deposition, the thickness of the samples in mechanical properties was (5µm) [11]:

$S=4Et_s^2D/3tL^2$ …… (4)

and

$D=d_1-d$ ……. (5)

Where D is the deflection where d_1,d_2 is the measurement that taking before and after deflection at the free end of the substrate in microscope(after deposition), E Yongs moduls of copper alloy substrate ,t film thickness ,L substrate length , t_s substrate thickness ,S internal stresses .The vickers microhardness was measured with (5g load) by using following relation[17]:

$H.v=1854.4\ p_f/d^2$ …… (6)

Where p_f is the load and d is the average diameter of the trace.

3. Results and discussion

Figure (2) shows the XRD charts of electroplated Ni-Co alloy thin films where (a) is 0M,(b) 0.02M,(c)0.05M,(d)0.1M and (e) 0.2M .We can see sharp peak of polycrystalline thin films and some small peak to the brass alloy substrate ,also we can see that in (a) pure Ni thin film electrodeposited from chloride bath mainly consisted of fcc phase with [(111), (200)and (220) planes], the domain peak at (111) , in (b) no peak was appeared to the Co ,because of the small amount of Co was actually deposited with Ni atoms at substrate surface ,which was founded about (5wt% of Co)only by chemical analysis ,and as we will see later in figure 3.The first apparent to the Co in the x-ray diffraction chart was at (c) which is represent(18wt% of Co)(figure 3)and in (d)a clear apparent to the Co peaks in the chart, domain peak to the Co at(e) with hexagonal phase and we can discriminated many planes [(100),(002),(101)and (110)] ,which agree with ASTM card number (Ni 04-0850),(Co 01-1278).Figure (3) shows the chemical analysis of NiCo alloys thin film after dissolving it from brass alloy substrate ,the figure represent a relation between the amount of Co in the solution and the real deposited amount in the films and we can see elevation in the deposition efficiency of Co by increasing Co concentration ,wile Ni content decreased .Figure (4)shows lattice mismatch(L.M) for the

deposited thin films with the brass alloy substrate which calculated from the relation [18]:

$L.M=2\left|a_2-a_1\right|/(a_2+a_1)$ …… (7)

Where a_1 is lattice constant for the brass alloy substrate and a_2 is lattice constant for the Ni-Co alloy thin films ,we can see that lattice mismatch in general have a small value due to the approach one another in atomic radius value for the deposited metals and substrate [18],an increment take place at first because of the low deposition ratio of Co atoms ,after that lattice mismatch decreased at higher deposition ratio [13,14].Figure (5) shows the relation of thin films grain size (G.S)and molarity of Co in solution, grain size was evaluated from the following relation [18]:

$G.S=K'\lambda/B\cos\theta$ …… (9)

where K' is about 1, B is the width of the half maximum(FWHM) ,we can see that the grain size also affected with molarity of Co. Grain size decreased relatively with Co percentage at(0.05M, 18wt% of Co) because this percentage represent the beast nucleation factor(agent)for arising grains and created thin film, so the texture became very fine and smooth ,as we will see later in figure (11)[9,10,14]. Figure (6) shows lattice strains which evaluated from the following relation [19]:

$\delta=\left|a_{ASTM}-a_{XRD}\right|/a_{XRD}\times100\%$ …… (8)

Where a_{ASTM} lattice constant from ASTM standard, and a_{XRD} lattice constant from X-ray spectrum, we can see that the lowest value was at 0.05M of Co, lattice strain decreased at that percentage due to the fine texture of the films and converge of the radius then increased as grain size increased .Figure (7) shows the relation of apparent density and theoretical density with changing the molarity of Co, apparent density was lower because of the natural of thin films growth which is included many internal vacancy inside the whole structure of the thin film, thin films perpetual have lower density compared with the bulk material ,also density decreased with Co because of growth mechanize. Figure (8) shows the changing in the open porosity with the molarity of Co, and it's in general decreased spicily at 0.05M of Co because of the finest texture and the whole substrate was covered with fine grains. Mechanical properties of this NiCo thin films was shown in figures (9, 10), where figure (9) shows the stress behavior of NiCo which is change from compressive stress to tensile stress at 0.05M of Co, this stress mode of NiCo thin films strongly depends on the composition ratio of deposited Co/Ni. However, film stresses are independent of deposit thickness [3],and this agree with[9,10],at compressive stress(below 0.05M) substrate deviance taken down and we taken the measurement before and after deviancy while at tensile stress(after 0.05M) substrate deviance taken up and we taken the measurement before and after deviancy, at (0.05M)the stress was zero no deviancy occur this manners related with alloy thin film content ,lower grain size and lattice strain .Figure (10) shows the microhardness behavior of NiCo which in general increased with increasing the molarity of Co, Co have a higher hardness in general increasing its ratio improve the microhardess[20,14] . Figure (11)

shows the effect of Co concentration on the surface morphology of NiCo alloy thin films, in (a) we can see the brass alloy substrate (uncoated),and (b) 0M,(c) 0.05M,(d)0.1M and in (e)0.2M of Co, we can see in (b,c) un orientated dispersion growth and in(d)an homogeneous fine nodular structure to dendritic structure ,in(e) became slightly pyramidal structure at 0.2M of Co and this variation in the texture because of the different in the Co deposition percentage (different alloy composition will deposited)[10,20], (f)shows microscope ruler(X200).

4. Conclusions

1-Magnetic NiCo alloys thin films were prepared from chloride baths with different molarity of Co on brass alloy substrate using electrodeposition method.

2-The domain orientation of Ni pure thin film at (111) change to(101) for NiCo with increasing Co contents(Ni/Co).

3- Ni,Co concentration change with molarity of them in the solution .

4-Density and open porosity decreased in general with Co concentration increased.

5-The transition of film stress from compressive to tensile at 0.05M (18wt% Co) may have resulted from the change of microstructure of it.

6- Microstructure also changes with Co concentration.

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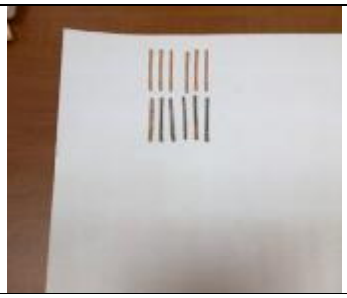
Table (1) composition of brass alloy substrate.

Element	wt%
Cu	95.02
Mg	0.1
Fe	0.02
Cr	0.05
Zn	4.29
Si	0.02
Sn	0.4

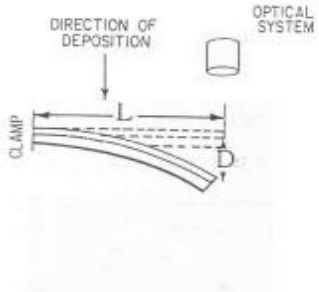
Table (2) Bath electrolyte compositions and parameters for Ni-Co films [15].

Solution of the bath	Concentration (M)	Deposition Parameter	
$NiCl_2.6\ H_2O$	0.2	pH	4
$CoCl_2\ .6\ H_2O$	0-0.2	Temp(°C)	60
H_3BO_3	0.4	Time(min)	10
NaCl	0.2	Current density	10 mA/cm^2



a-Samples before and after deposition.

b-Electrodeposition unit.



c- Bending beam method.

Figure (1)

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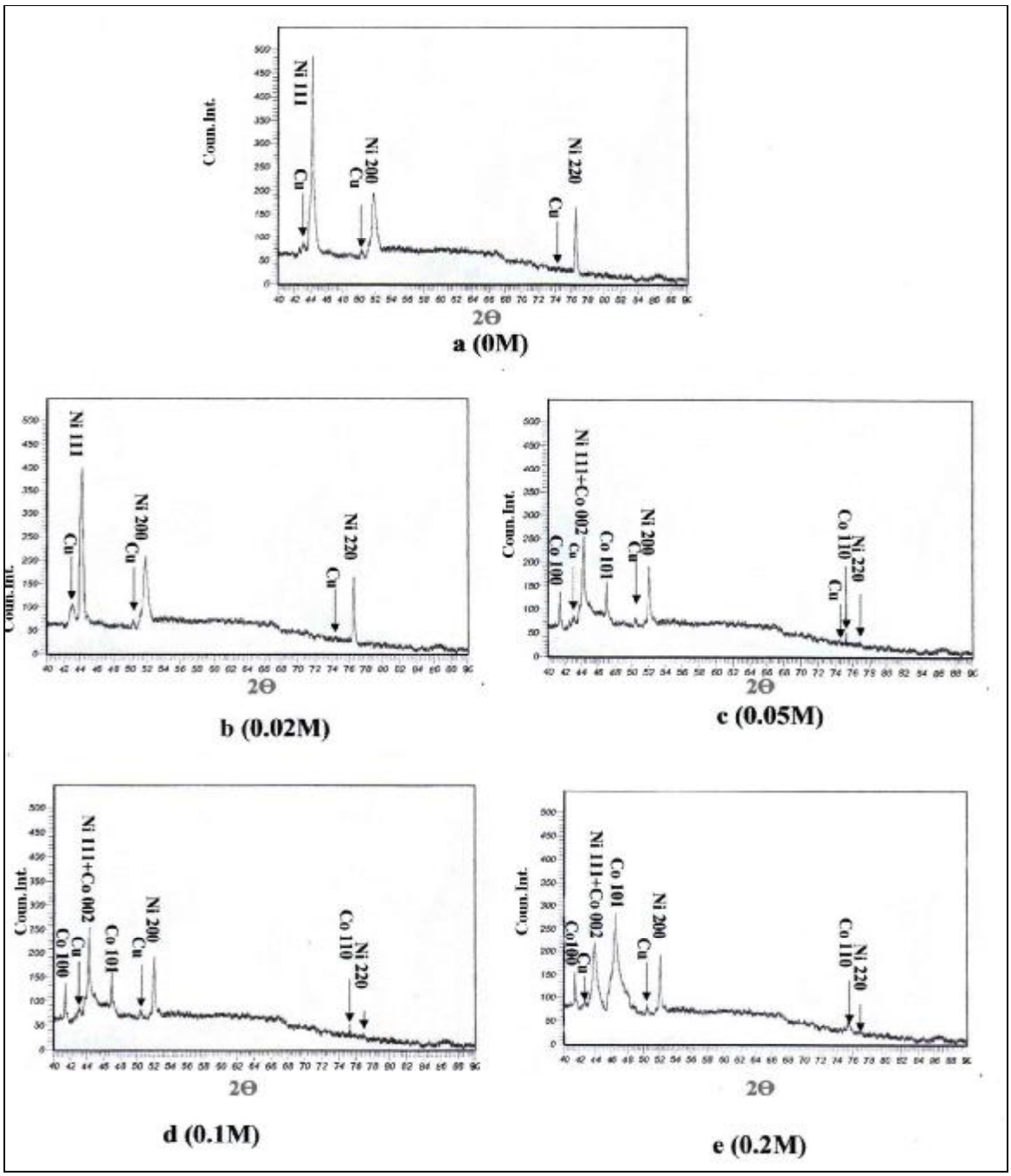


Figure (2) XRD spectra of NiCo thin film alloy.

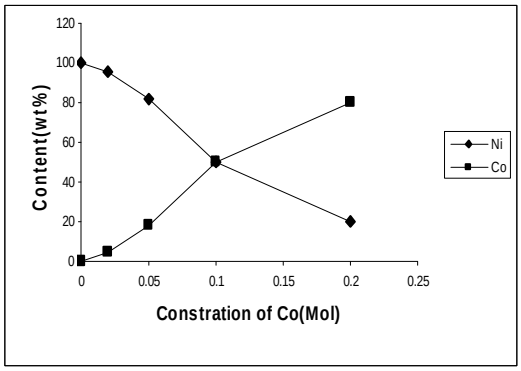


Figure (3) NiCo thin film alloy contents and the concentration of Co.

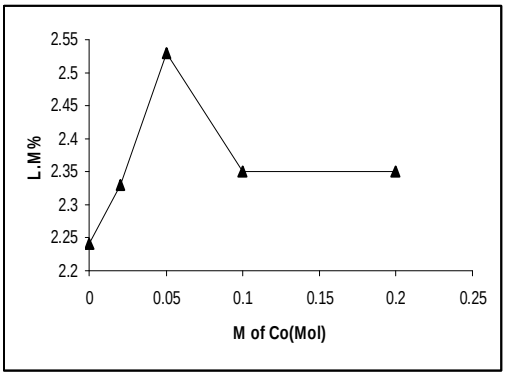


Figure (4) Relation between lattice mismatch and the molarity of Co.

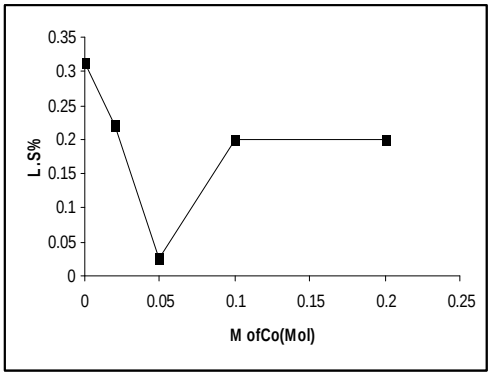
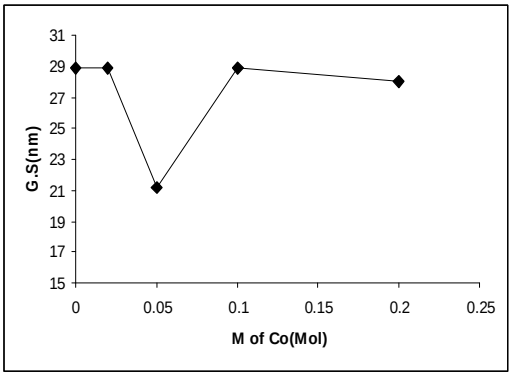


Figure (6) Relation between lattice strains and the molarity of Co.



Figure(5) grain size of NiCo thin film alloy and the molarity of Co.

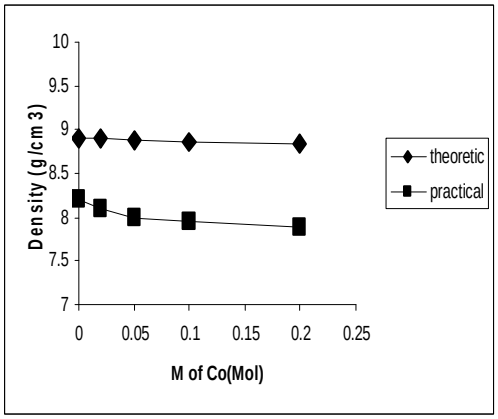


Figure (7) Apparent density of NiCo thin film alloy the molarity of Co.

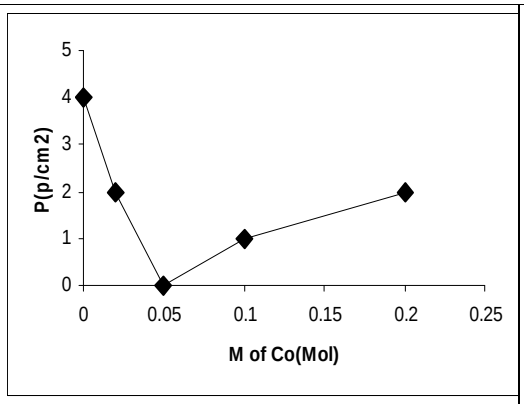


Figure (8) Open pores in NiCo thin film alloy on copper substrate the molarity of Co.

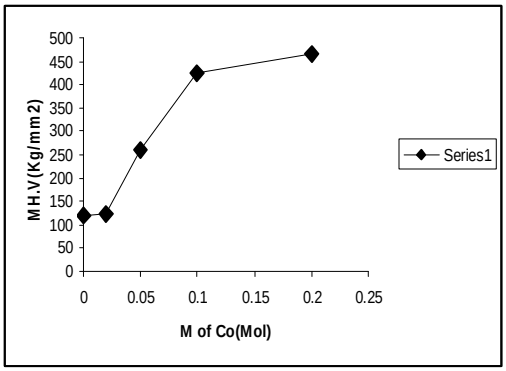


Figure (10) microhardness ofNiCo thin film alloy the molarity of Co.

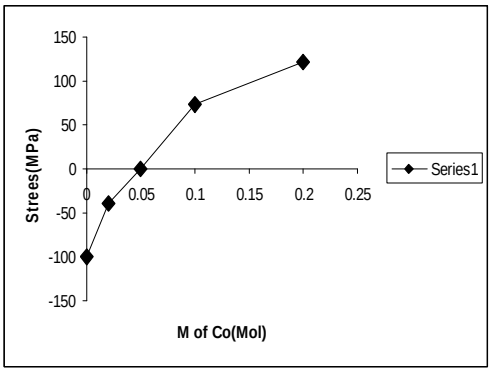
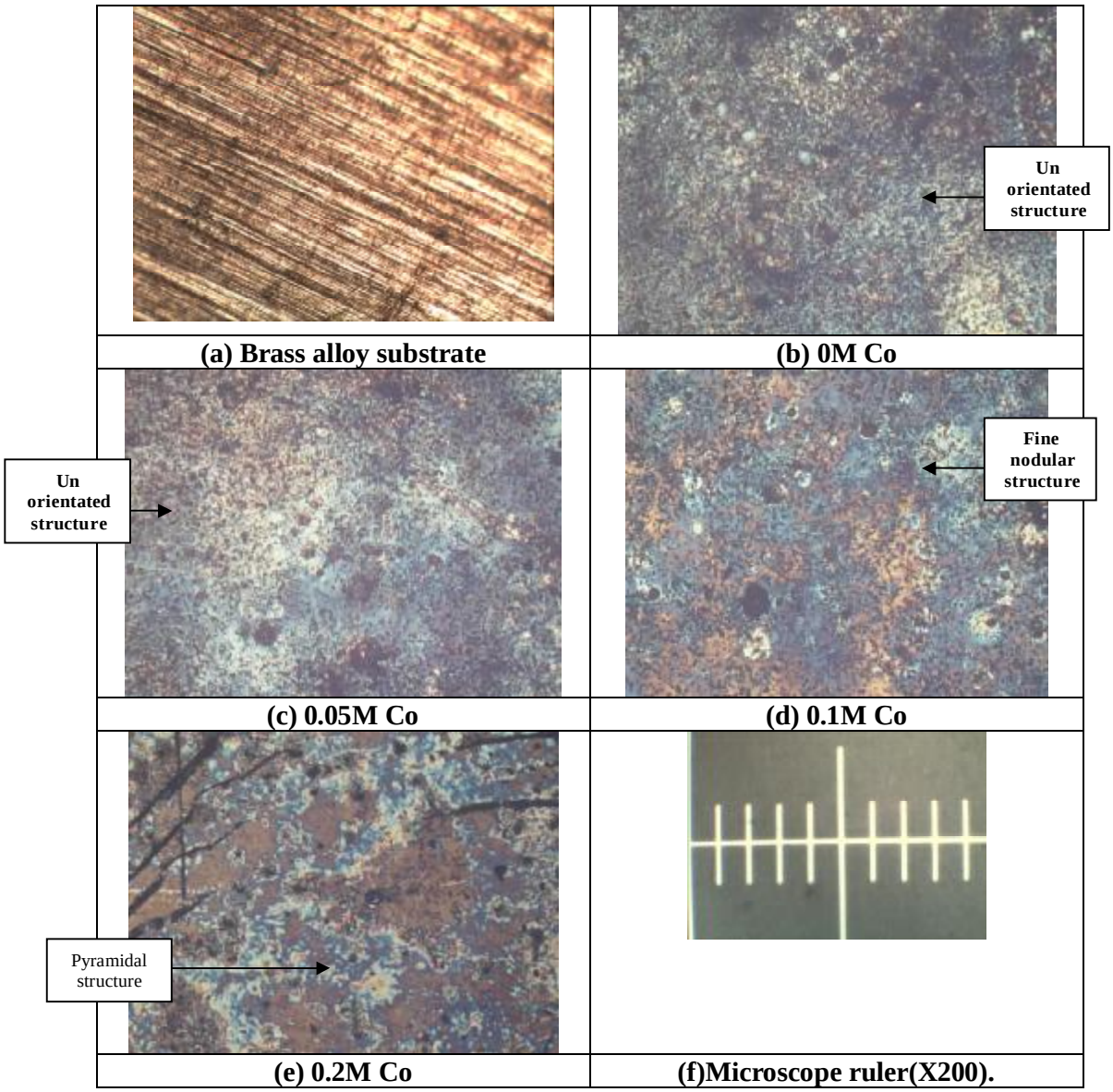


Figure (9) stress of NiCo thin film alloy the molarity of Co.



(a) Brass alloy substrate | (b) 0M Co

(c) 0.05M Co | (d) 0.1M Co

(e) 0.2M Co | (f)Microscope ruler(X200).

Figure (11) Surface morphology of NiCo thin film alloy X200.