THE ANNALS OF "DUNĂREA DE JOS" UNIVERSITY OF GALAȚI
FASCICLE V, TECHNOLOGIES IN MACHINE BUILDING, ISSN 1221-4566
2008

Doping Effect on Texture Degree of a Nanocomposite Layer

C. GHEORGHIES[1], D. HUI[2], V. PAUNOIU[1]
[1]Dunarea de Jos University, Galati, RO 800008, Romania
[2]University of New Orleans, New Orleans, LA 70148, USA

ABSTRACT

The knowledge of the texture into bulk material or thin films is very important taking in account the relationship between the orderly arrangement of atoms or molecules and some physical, chemical, mechanical or metallurgical properties of materials. In this paper a method of preparation of a nanocomposite layers consists in a nickel matrix where ceria particles were added and the estimation of the texture degree of them by X-ray diffraction method using rocking technique of sample carried out point.

Keywords: *electrocodeposition, nickel matrix, ceria particles, texture, X-ray diffraction*

1. Introduction

The knowledge of the texture into bulk material or thin films is very important taking in account the relationship between the orderly arrangement of atoms or molecules and some physical, chemical, mechanical or metallurgical properties of materials.

By X-ray diffraction method the influence of concentration of doping element on texture degree of nanocomposite thin films is presented [1]. Important material properties, such as residual polarization, dielectric constant and elastic module, are typically anisotropic, and the most effective use of anisotropic materials in thin film applications often involves controlling the texture of the films or layers.

2. Experimental material

The composite layers in nickel matrix were electrodeposited from electrolytes with the composition mentioned below and added ceria particles in the plating bath.

The nickel deposition took place in a Watt's electrolyte: 0.90 M $NiSO_4 \cdot 6H_2O$; 0.20 M $NiCl_2 \cdot 6H_2O$; 0.28M H_3BO_3 and 0.4g/l $CH_3(CH_2)_{11}OSO_3Na$. The pH value of the electrolyte was 4.2 – 4.5 by careful correction during the entire deposition processes [2, 3]. The experiments were performed at 50 – 55 $^{\circ}C$ temperature.

Ceria as dispersed phase with a particles size of around 1 μm and concentrations between 25 and 100 g/l was added. To keep the particles in suspension the electrolyte was magnetically stirred with 700 rpm.

The co-deposition experiments were performed in the galvanic mode to carry out the optimal conditions of suspended particle concentration, pH and current density. Pure nickel as anodes were used placed in a distance of 50 mm from the cathode surface performed from carbon-steel. A current density between 2 – 5 A/dm^2 was applied. Due the number of variables which affect the resulting deposits three separate experiments were prepared [4]. The thickness of deposits measured at the cross section varies depending of the electrolysis conditions. We obtained a thickness between 50-80 μm.

3. Working methodology

In order to estimate the level of texture in obtained thin films an X-ray diffractometer giving an incident X- radiation of 1.541 Å equipped with a monochromator in diffracted X-ray. There are certain problems peculiar to

the measurement of texture in thin films, the most significant of which is that the intensity of diffracted X-rays that can be obtained from a thin film is frequently so small that intensity measurements are of low accuracy.

Thin films deposited on planar substrates typically display fiber texture with the substrate normal as the fiber axis. Substrates patterned with surface features such as trenches for conduction vias may display more complex, three dimensional textures.

The q scan gives the variation of scattered intensity with specimen orientation and contains the required texture information, but it must be corrected for defocusing and absorption to obtain the texture profile. In a pole figure measurement, this is typically achieved by measuring a specimen of the same phase composition but with no preferred orientation (i.e. a random specimen) and dividing the intensity from the textured specimen by that from the random specimen, thus obtaining multiples of a random distribution, MRD, as a function of specimen orientation.

In the technique of Vaudin et al., the scan that would be obtained from a random specimen is calculated from the $q-2q$ scan of the Bragg peak, taking into account defocusing and absorption, and the texture profile is determined by dividing the experimental scan by the calculated random scan. In this way, the shape of the texture profile is determined, but the scaling is arbitrary [5].

The technique required the recording of two scans from the sample: a high resolution $q-2q$ scan of a Bragg peak whose diffracting planes are normal to the preferred orientation direction; and a q scan obtained using this peak.

Figure 1 presents the irradiation schema of specimen in order to study the texture degree of Ni/ceria coatings. It can observe the presence of a defocalization of the X-ray beam that negatively influences the diffracted intensity. This influence can be annihilated by using certain correction formula presented by Vaudin in paper [5].

Fiber thin film texture implies the preferential alignment of a particular set of crystal planes parallel to the substrate. The data collected from the specimen are the two X-ray scans described above, $I_{pk}(2q)$, a $q-2q$ scan of a Bragg peak appeared at Bragg angle noted q_B from the aligned planes, and a scan, $I_{rc}(w)$, where the specimen orientation is tilted away from the symmetric orientation through about an axis in the specimen surface normal to the diffraction plane, while the scattering angle remains fixed at $2q_B$.

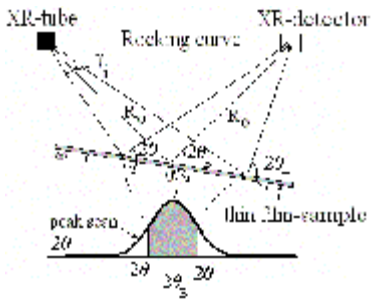

Fig. 1 –Irradiation schema of Ni/ceria coating

The scan for a randomly oriented specimen of the same material, $I_{rd}(w)$, is calculated from $I_{pk}(2q)$ by correcting for defocusing and absorption, and the texture profile, $T(w)=\frac{I_{rc}(w)}{I_{rd}(w)}$, is calculated. As the specimen is tilted away from the symmetric orientation in either direction, the X-ray scattering angle, $2q$, varies along the irradiated length of the specimen.

The central assumption of the theory is that the intensity of a ray scattered by the specimen through $2q$ is proportional to the $q-2q$ scan intensity at angle $2q$. Thus, the q scan intensity at angle w is proportional to the integral of the Bragg peak intensity, as illustrated in figure 1; the scattering angle variation is in range $2q_{-}<2q<2q_{+}$.

The integral intensity is carried out as a function of $g\in\left[-\frac{g_i}{2},\ \frac{g_i}{2}\right]$ and therefore it can be written:

$$I_{rd}(w)\ !\ \frac{1}{g_i}\int_{-\frac{g_i}{2}}^{\frac{g_i}{2}} I_{pk}\left[2q(w,g)\right]dg \qquad (1)$$

where g_i is the divergence of the incident beam and g is the current divergence of an X-ray from the central ray. The factor that determines the constant of proportionality in the above relation is absorption.

From simple geometry, an X-ray striking the specimen surface at angle f.. penetrating to depth z in the thin film sample, scattering through $2q$ and returning to the surface is

attenuated by the factor $k(z, f, 2q)$ given by relation:

$$k(z, f, 2q) = \exp\left[-mz\left(\frac{1}{\sin f} + \frac{1}{\sin(2q - f)}\right)\right] =$$

$$= \exp\left[-mz\,D(2q, f)\right] \quad (2)$$

where m is the linear coefficient of X-ray absorption, and $f = q_B + w - g$ representing the angle of incidence of the X-ray on the specimen surface.

For an X- ray having an incidence given by angle g, on a film of thickness t, the total effect of X-ray absorption on the recorded intensity is found by integrating through the thickness of the film, namely:

$$A(w, g) = \int_0^t k\left[z, f(w, g), 2q(w, g)\right] dz =$$

$$= \frac{1 - \exp\left[-m\,D(2q, f)\,t\right]}{m\,D(2q, f)} \quad (3)$$

To relate I_{pk}, the intensity measured at zero tilt, to the intensity that would be measured during a scan when the specimen tilt varies, the I_{pk} values are first divided by $A(0, g)$ and then multiplied by $A(w, g)$, giving the correction factor:

$$F(w, g) = \frac{A(w, g)}{A(0, g)} \quad (4)$$

and results:

$$I_{rd}(w) = \frac{1}{g_i} \int_{-\frac{g_i}{2}}^{\frac{g_i}{2}} F(w, g)\, I_{pk}\left[2q(w, g)\right] dg \quad (5)$$

Thus, measuring I_{pk} and I_{rc} the texture profile $T(w)$ can be calculated. Agreement between them is a good check on the reliability of the data. The units of $T(w)$ can be found by considering that when $w = 0$, but $2q$ varies very little with g (only by the flat specimen correction), and therefore from last relation results that $I_{rd}(0) = I_{pk}(2q_B)$ with a very good approximation. Since, within experimental error, $I_{pk}(2q_B) = I_{rc}(0)$, it can be seen that within experimental error $T(0) = 1$. As w increases, $T(w)$ decreases from 1 for positively textured samples. If $T(w)$ were known over all orientation space, the profile could be scaled to be in MRD by multiplying by the MRD value at $w = 0$, MRD_0 which can be found from the normalization condition:

$$\int_0^{\frac{p}{2}} MRD_0\, T(w) \sin w\, dw = 1 \quad (6)$$

With this rocking curve technique, is limited to a range: $0 < w < q_B$. However, last equation can still be used in those cases where the texture profile of a material is narrow enough that it decays to zero within the observed orientation range and can be assumed to be zero in the unobserved orientation range.

4. Experimental texture control

The technique has been designed to be used with a conventional divergent beam X-ray diffractometer. The two X-ray scans collected, the $q - 2q$ scan and q scan, were collected under identical conditions; in particular, the incident and receiving slits were the same.

Figure 2 shows a SEM image of Ni/CeO_2 thin film prepared from bath with 5 g/l CeO_2 (a), and 50 g/l CeO_2(b), at 3 A/dm^2.

Figure 3 displays an X-ray difractograme of a Ni/CeO_2 thin film and figure 4 the texture profile of the same coating taking in consideration the crystallographic planes (220) for nickel matrix having, respectively, the following ceria concentration: 0 g; 5g; 10g; 50g and 100g per liter.

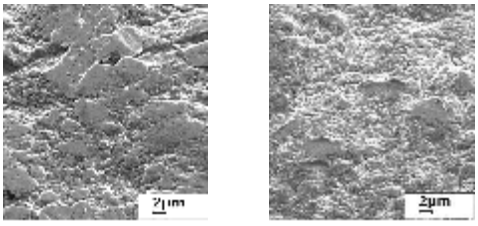

Fig. 2 – SEM images of Ni/ceria thin films (left-5g/l ceria; right-50g/l ceria)

It can see how influence the ceria concentration on orientation degree of the crystallographic planes noted (220) appertaining to nickel matrix in composite layer. An increasing of (220) planes density in various section of composite layer, having a maximum value at a plane doing with the surface for angles ranged between 40 and 50 degrees is showed.

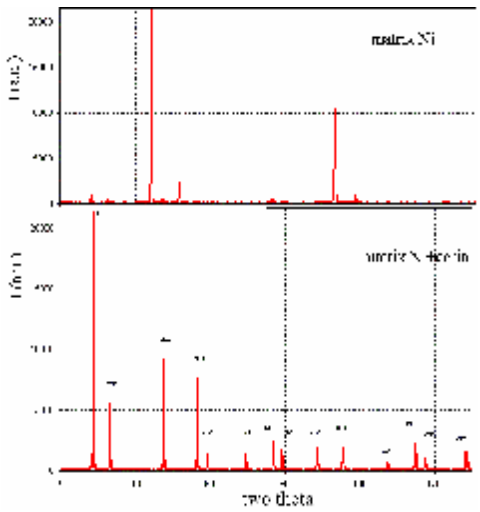

Fig.3-X-ray patterns of composite Ni/ceria layer

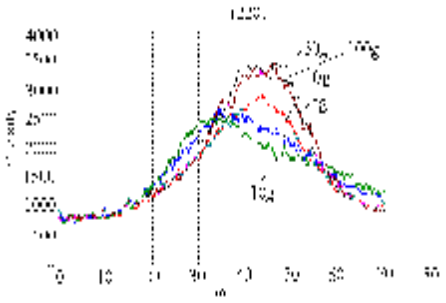

Fig.4- Texture degree vs. ceria concentration

5. Conclusions

The presented results allow conducting the electrodeposition process by means of ceria concentration in order to obtain certain structure inside of Ni/ceria composite thin film.

The nanoparticles appear agglomerated in the layers of a nickel matrix without having a crystalline structure. Additions of alumina particles with a particle size of 20 nm of 5 g/l and 10 g/l into nickel plating bath change the preferred growth direction of the electrodeposited nickel from <100> to <111>. This change is not induced by the epitaxial effects of substrate, which show a predominant (111) reflection, or by the presence of alumina in the bath. The microstructure of composite coatings is changed in comparison with pure nickel deposits, when alumina was added.

References

[1] **Gheorghies, C.,** *Analiza structurii fine a materialelor*, Ed. CERMI, Iasi, 2007.

[2] **Yeh, S. H., Wan, C. C.,** *Electrochemical investigation of the codeposition of SiC and SiO2 particles with nickel*, J. Appl. Electrochem. **24**, 993, 1994.

[3] **Jang, J.S.C., Chang, L.J., Young, J.H., Huang, J.C., Tsao, Chi Y.A.,** *Synthesis and characterization of the Mg-based amorphous/nano ZrO_2 composite alloy*, Intermetallics, Volume 14, Issues 8-9, August-September, 2006.

[4] **Qu, N.S., Zhu, D., Chan, K.C.,** *Fabrication of Ni–CeO_2 nanocomposite by electrodeposition*, Scripta Materialia, vol. 54, 7, Aprilie, 2006.

[5] **Vaudin, M. D.,** *Accurate texture measurement on thin films using a powder X-ray diffractometer*, NIST, Gaithersburg, MD, USA, 1999.

Efectul dopării asupra texturii unui strat nanocompozit

Rezumat

In lucrare, se prezintă o metodă de obținere ale unor straturi nanocomposite care constau dintr-o matrice de nichel în care s-a adăugat particule de ceria, estimându-se influența acestora asupra gradul de texturare a filmelor subțiri obținute. În acest scop, s-a utilizat difracția de radiații X în tehnica scanării suprafeței prin rotirea probei în capul goniometric.

L'effet du dopage sur la texture d'une couche nano composé

Résumé

Dans ce papier on présente une méthode d'obtention des couches nanocomposites ayant comme base une matrice de nickel dans laquelle on ajoute du cérium et on estime l'influence du cérium sur la texture des couches minces. Pour cette analyse on a utilisé la diffraction des rayons X en scannant la surface par rotation de la couche en champ goniométrique.