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On the Model Calculation of the Excitonic-Like States and Their Possible Role in Autocatalytic Processes

I. Application to the Formation of Autocatalytic Ni-P Amorphous Coatings

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A new exciton-like excitation mechanism is suggested for the formation of amorphous Ni-P coatings based on the special spatial bonds of hydrogen ions on the surface.

Auf der Grundlage der speziellen räumlichen Bindungen der Wasserstoffionen an der Oberfläche wird ein neuer exzitonenähnlicher Anregungsmechanismus für die Bildung von amorphen Ni-P-Oberflächenschichten vorgeschlagen.

1. Introduction

The formation of metastable states, first of all in amorphous alloys has attracted a large interest for a long time.

The following of formation process of metallic glasses is rather difficult because of the very small formation time in the superquench process. The relatively slow plating rate and the possibility of step-by-step investigations make the electroless process one of the most useful models for studying formation effects [1]. In spite of these useful properties, two basic problems have arisen in real investigations [2]:

a) the chemical process has many unclear details, first of all, the autocatalytic effect has not yet been fully understood;

b) the electroless bath consists of some added components, so the sample purity in many cases is not high enough for scientific investigations.

The basic scientific problems of the electroless coating process are concentrated on the structural peculiarities of the formed binary alloy; namely, which type of phases has been constructed, what are the relevant parameters depending on the formation of metallic glasses.

The first formation step has been investigated by many authors [3 to 5]; but the role of different components at the nucleation, or the role of hydrogen which is intensively liberated during all the process, are not discussed. Some information is known about the incubation time [6], the changes of the composition [7], the very important role of the pH value [8], but their interdependence is not yet clear.

In some of our earlier publications we tried to clarify some details of the process and the effects of different chemicals in the electroless bath [9]. Using these results, a new picture is suggested for the forming, based on the electronic structure and special electronic states of the alloy.

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In our recent paper a model based on an exciton-like state constructed by a proton in a vacancy with the special screening process of electronic states is suggested.

This model has become so helpful for the explanation of the electroless autocatalytic process that we can imagine a wider application of the model in the field of surface effects, including catalysis.

2. Theoretical Basis

Based on Frenkel's well-known vacancy theory for the melting of metals [10] a special deposition process can be assumed, in which in a quasi-binary alloy in the first step a cluster of nickel atoms is produced of vacancies and chemically reduced atoms. The general binary rule for the Ni-Va (Va vacancy) quasi-binary alloy is

$$c_{\text{Ni}} + c_{\text{Va}} = 1,$$

where c_{Ni} and c_{Va} are the concentrations of nickel and vacancies, respectively. Parallel with the effect of minimizing the energy in all stages of this nonequilibrium process there must be equilibrium with the bath of electroless solution at a constant temperature. The process is isothermal and the corresponding average can be given for the system. The general electronic theories of solids can be used for the surface energy and the bonding energy, too, for the determination of the spatial flow of different components.

The Hamiltonian of the system can be given in the following form:

$$H = H_0 + H_{\text{int}}, \quad (1)$$

where H_0 is a simple Hamiltonian for the binary alloy, and H_{int} gives a new effect, the interaction of the hydrogen ions (protons) with the system,

$$H_0 = \sum_{i,j} t_{ij} a_i^\dagger a_j + \sum_i V_i n_i,$$

where t_{ij} is the integral of the electron jump from the i -th place to the j -th one, a_i^\dagger and a_j the operator of second quantization at the i -th and j -th site, respectively, V_i the potential of the i -th site, where the number of electrons is n_i .

The solution of the Schrödinger equation constructed by the simple Hamiltonian (H_0) is a difficult task in the general case, but it seems to us that the CPA (coherent potential approximation) method approaches reality well for solving the problem.

In the first step the Coulomb-type interaction between the vacancies and the captured protons is switched off and in the second step the Coulomb interaction is switched on in the form of a local excitation in the system.

According to Fukuyama and Ehrenreich's results [11] in this picture the difference of atomic potentials of the transition metal and the vacancy is so large, that we can assume

$$\frac{E_{\text{M}} - E_{\text{Va}}}{w} \gg 1,$$

where E_{M} and E_{Va} are the atomic energies of the transition metal and the vacancy, respectively, and w is a band-width of the unperturbed "d" band.

In this case the density of states of H_0 is smoothed, has no fine structure, and consequently, the important features of the density of states of the components can be approximated by CPA as follows [12, 13]:

$$\rho_i(\varepsilon) = \frac{4}{\pi w \sqrt{c_i}} \left[1 - \left(\frac{2(\varepsilon - \alpha_i)}{w \sqrt{c_i}} \right)^2 \right]^{1/2}, \quad (2)$$

where c_i and α_i are concentration and energy of the atomic level of different components, respectively. The bonding energy of the different components of the given 'quasi-alloy' can be written in the frame of the Hartree picture [14] as

$$E_i = \int_{-\infty}^{E_F} (\alpha_i - \varepsilon) \rho_i(\varepsilon) d\varepsilon, \quad (3)$$

where E_F is the Fermi energy which can be determined from the condition

$$n = \sum_{i=1}^N \int_{-\infty}^{E_F} c_i \rho_i(\varepsilon) d\varepsilon \quad (N = 2). \quad (4)$$

The average concentration of electrons (n) in our simple case is equivalent to the average number of d electrons of nickel, because the electron concentration of vacancies is equal to zero ($n_{va} = 0$).

Using (2) and (3) we obtain

$$E_i = \frac{2}{3\pi} w \sqrt{c_i} \left[1 - \left(\frac{2(E_F - \alpha_i)}{w \sqrt{c_i}} \right)^2 \right]^{1/2}, \quad (5)$$

and from (4) with high accuracy

$$E_F \approx \alpha_i + \frac{w}{2} \sqrt{c_i} (n_i - 1); \quad n_{TM} = \frac{n_d}{5}. \quad (6)$$

n_{TM} and n_d are the relevant numbers of electrons of transition metal and the "d"-symmetries, respectively (in our case, TM = Ni).

Consequently,

$$E_i = \frac{2}{3\pi} w \sqrt{c_i} [n_i(2 - n_i)]^{1/2}, \quad (7)$$

which can be used for the metal-vacancy quasi-binary alloy, according to H_0 ,

$$E_0 = \frac{2w}{3\pi} \{ [n_{Ni}(2 - n_{Ni}) c_{Ni}]^{3/2} + [n_{va}(2 - n_{va}) c_{va}]^{3/2} \}. \quad (8)$$

The second term of the Hamiltonian (H_{int}) can be determined by the known solution for hydrogen-like systems [15]. Considering the specific screening potential in the case of metals, the total energy is

$$E_{int} = \frac{m^* e^4}{2\hbar m^2} \exp(-2\lambda a_H) c_{va}, \quad (9)$$

where m^* is the effective mass of electrons in the metal, e the charge of the electron, n the mean quantum number (in the following, $n = 1$), and a_H the Bohr radius. The λ -parameter is determined by the screening at the interaction of the proton (H^+) captured by the vacancy. In the case of d-metals this is equal to [15]

$$\lambda = (4\pi e^2 \rho(E_F))^{1/2}, \quad (10)$$

where $\rho(E_F)$ is the density of states at the Fermi energy. In the case of Ni-P metallic glasses the average distance parameter is $a = 0.354$ nm and $\rho(E_F) \approx 1/eV$ [16]. In this case $\lambda = 0.17$ nm⁻¹, which is lower than the relevant factor, e.g. the reciprocal

value of the Bohr-radius,

$$\lambda < a_{\text{H}}^{-1}, \quad (11)$$

which corresponds to a bound state of a proton [16]. The bound state is connected with a relatively high $\rho(E_{\text{F}})$ and represents a direct proof for the existence of the bound hydrogen-like state corresponding to H_{int} . The capture of electrons by the protons produces an excitonic-like state, characterizing the interactions of the electrons with the corresponding electron vacancies in the conduction band of the quasi-alloy.

The energy of this state can be easily calculated from (9), using the m^* -value corresponding to the average effective mass of the electron-hole pair [15].

In this case

$$E_{\text{e-h}} \approx 0.125 \text{ eV} .$$

which is obviously stable below 1000 K. The characteristic radii of the excitonic-like state are in our case

$$a_{\text{e-h}} \approx 12 \text{ nm} .$$

This means that the excitation connected with the existence of the electron-hole excitonic-like states has a large, long-range effect (nearly ten atomic distances). In the case of a few excitonic-like pairs the excitations are delocalized in the whole crystal.

In crystalline materials the spreading of excitons is very similar to the moving of magnons in ferromagnets, and in the translation-invariant case they have wave-like states. In our case we conclude that the excitonic-like state in amorphous materials in the frame of the effective medium approach has a form very similar to that in crystals.

The total energy of the system is obviously the sum of the above-calculated terms,

$$E = E_0 + E_{\text{int}} . \quad (12)$$

Taking the real concentration of vacancies $c_{\text{v}} \approx 0.1$ [10] and so $E_{\text{int}} \approx 2.4 \times 10^{-2} \text{ eV}$, which is a small fraction of the given d-band energy (1 to 5 eV), the additivity of the terms is confirmed.

The surface segregation can play a modifying role in the system.

The average coordination number in the first coordination sphere on the surface (z_{s}) of vacancy-rich metals (quasi-binary alloys) is smaller than in the bulk (z_{v}) [14, 17].

Therefore, the surface energy using the condition for the bonding energy (5) is as follows:

$$\gamma_i = E_{\text{v}}^i - E_{\text{s}}^i = \left[1 - \left(\frac{z_{\text{s}}}{z_{\text{v}}} \right)^{1/2} \right] \frac{2w}{3\pi} [n_i(2 - n_i)]^{3/2}, \quad (13)$$

and the energy of segregation of the metal-vacancy quasi-binary alloy will be

$$\begin{aligned} \Delta E &= \gamma_{\text{Ni}} - \gamma_{\text{Va}} = \\ &= \left[1 - \left(\frac{z_{\text{s}}}{z_{\text{v}}} \right)^{1/2} \right] \frac{2}{3\pi} \{ [n_{\text{Ni}}(2 - n_{\text{Ni}})]^{3/2} w \sqrt{c_{\text{Ni}}} - [n_{\text{Va}}(2 - n_{\text{Va}})]^{3/2} w \sqrt{c_{\text{Va}}} \} . \end{aligned} \quad (14)$$

3. The Model

A model can be based on the previously calculated results for the formation process of the amorphous state of a Ni-P binary alloy.

The binding energy of nickel atoms, as is obvious from (8), decreases by the incorporation of vacancies into the coating layer,

$$E(c_{v_n} \neq 0) < E(c_{v_n} = 0); \quad n_{v_n} = 0.$$

The adhesive forces between nickel and the substrate atoms are not changed and remain typical for the two given materials. During the formation of nickel clusters on the substrates, the coating of nickel atoms starts a parallel process, namely the segregation of defects (vacancies) to the surface ($n_{v_n} = 0$ and $\Delta E > 0$). Opposite to the direction of the vacancy flow towards the surface, a phosphorus deposition is observed together with the continuous nickel deposition.

The process is proved by experiments elsewhere [7]. The Ni-cluster formation in the first step and the continuous flow of phosphorus atoms are observed by the intensity ratios of Ni and P SXES spectra. The change of subplaces of $L_{2,3}$ spectra of phosphorus during the process of electroless coating is also characteristic, showing the growth of a new peak at the Fermi edge corresponding to $s + d$ hybridization and bonding of the phosphorus. This process increases the bonding energy of the alloy (cf. (3), too).

Recently a new KKR-CPA calculation [16] showed the mechanism of the changes of the electronic structure during the formation of Ni-P amorphous alloy: the "p" states of phosphorus interact with the $s + d$ hybridized states on the top of the d-band of Ni constructing a new pd-bonding and a pd-antibonding type state below and above the Fermi level, respectively.

4. Discussion

According to our measurements the start of the electroless process is the production of pure Ni clusters in the case of all electroless baths and substrates. The chemical reaction of nickel deposition is accompanied by an intensive reduction process basically operated by hydrogen and, consequently, by a considerable hydrogen gas liberation.

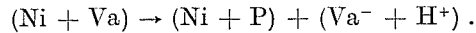
Based on the above-described model calculation, the autocatalytic process of the amorphous coating becomes clearer. The first step of the process is the hydrogen ion capture at the substrate. In the case of nonmetallic substrates we must use a catalytic metallic solution for the first nucleation step which is generally PdCl_2 [3]. The hydrogen overvoltage of the metal in the aqueous solution must decrease (the work function decreases [18]) and the captured hydrogen ion is observed on vacancy sites and forms excitonic-like states in d-metals.

This acceptor-like level with a very large correlation length helps to capture another hydrogen ion into the vacancy site. The exciton as a Bose-Einstein particle can condense. In the case of non-transition element substrates first a few Ni atoms are electrolyzed onto the surface by the external sources, which can represent the starting step. On the vacancy places of the Ni clusters a proton is captured forming an excitonic-like state. This excitonic-like excitation has a long correlation distance and gives a possibility to capture Ni atoms; these, in turn, produce still more vacancies, and more excitonic-like states, too. The absorbed hydrogen can be desorbed at a definite critical value of the concentration and by the net hydrogen atom, they are liberated as H_2 gas.

The nucleation centre is an active site on the uncoated surface. The growth of amorphous media is homogeneous and isotropic, so it should be spherical (semi-spherical). Then the whole surface of the spherical nucleus must be in the same active state, associated with the formation of a continuous layer on the surface of the nuclei.

The excitonic-like states on the whole surface are in the same energy state because of the Bose-Einstein statistics of these quasi-particles. The overlapping of the "sensitive" excitonic-like areas can lead to a continuous two-dimensional "active" surface. During the growth process the nucleation work is increased, and after having reached a critical value [19], a new sphere begins to form on the surface of the old one. This has been observed experimentally [7].

The flow of different atoms at the forming process is accompanied with a well-defined charge transfer. The charge flow caused by the vacancies is neutralized by the hydrogen ions. The schematic description of the process based on the neutralization charge transfer is



The capture of phosphorus to the system disturbs the electron-hole-proton system, the long-range correlation vanishes, and the phosphorus atom is fixed at the place where the absorption happened. This means that an amorphous-like structure has been constructed growing isotropically [4].

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