KINETIC OF FORMATION OF NONMAGNETITE LAYER ON SURFACE OF MAGNETITE NANOPARTICLES IN ITS PREPARATION BY CHEMICAL PRECIPITATION METHOD

RASIM A.ALI-ZADE

Institute of Physics Azerbaijan National Academy of Sciences

Existing of non-magnetite layer in magnetite nanoparticles obtained in different conditions of chemical precipitation of solution of 2 and 3 valences of iron salts by surplus alkali has been established. Mechanism of formation of non-magnetite layer in the surface of magnetite nanoparticles, dependence of thickness of non-magnetite layer from size and condition of preparation of magnetite nanoparticles has been investigated.

1. INTRODUCTION

At present existing of non-magnetite layer in magnetite nanoparticles has been established by different authors [1,2]. However, problem of mechanism of formation and nature of non-magnetite layer in magnetite nanoparticles don't investigated. These investigations are necessary to obtain information allowed controlling of preparation of magnetite nanoparticles, receiving nanoparticles with early given size and properties.

The present work is dedicated to the investigation of mechanism of formation of non-magnetite layer in the surface of magnetite nanoparticles.

2. THEORY

2.1. Establishment of existing of non-magnetite layers in the surface of magnetite nanoparticles and determination of its thickness.

At early experimental magnetisation curves of samples of magnetite nanoparticles at different concentration of magnetite was been investigated [1-3].

Magnetization curves of samples I, III of magnetite nanoparticles by average diameters of nanoparticles 9.48 and 7.3 nm at concentration of solid phase $\varphi_g = 0.012$ and 0.011 obtained by experimental and calculated by Langevin equation respectively are showed in fig.1 (a,b). As see experimental values of saturation magnetisation of samples I and III ($M'_{s,\exp} = 0.327 \cdot 10^4 \, A/m$, $0.384 \cdot 10^4 \, A/m$, correspondingly) and calculated its value ($M'_{s,theor} = 0.549 \cdot 10^4 \, A/m$, $0.523 \cdot 10^4 \, A/m$,) are not agree [1-3].

Langevin equation at big value of magnetic field may be write as $M'_{s,\exp} = M'_s \varphi_g$ (M'_s is saturation magnetisation of bulk magnetite) and φ_g calculated from correlation of $M'_{s,\exp} / M'_s$ for these samples is equal to 0.007, 0.008 correspondingly and don't equal to φ_g, indicated above (0.012 and 0.011). We suggested, that geometrical size of nanoparticles (d_g) not is equal to magnetic size of nanoparticles (d_m) and nanoparticles have non-magnetite layer ($d_m = d_g - x$). Use expression of concentration solid phase for correlation of solid and magnetic phase we obtain $\varphi_g / \varphi_m = \overline{d_g^3} / \overline{(d_g - x)^3} = \alpha$ where over line of parameters is indicated to its average value. At writing this expression we also suggested, that all nanoparticles of medium have non-magnetite layer. After transformation of expression of correlation of concentration get following cubic equation

$$\overline{x^3} - 3 \cdot \overline{d_g x^2} + 3 \cdot \overline{d_g^2 x} - (1-\alpha)\overline{d_g^3} = 0 \qquad (1)$$

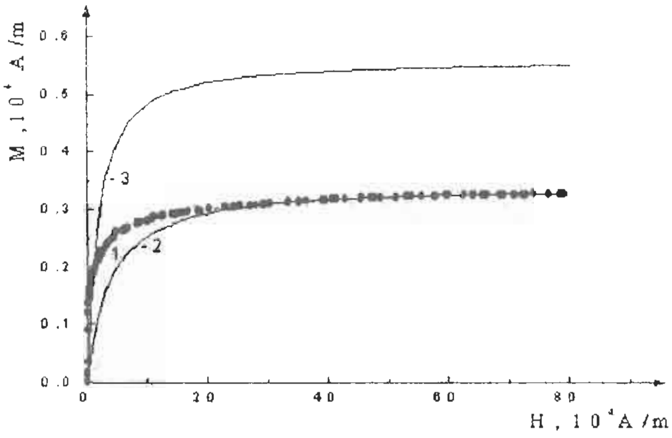

Fig.1a Magnetisation curves of sample I at $\varphi_s = 0.012$ obtained experimental (curve 1), by Langeven equation without and with take into account non-magnetite layer (curves 2,3).

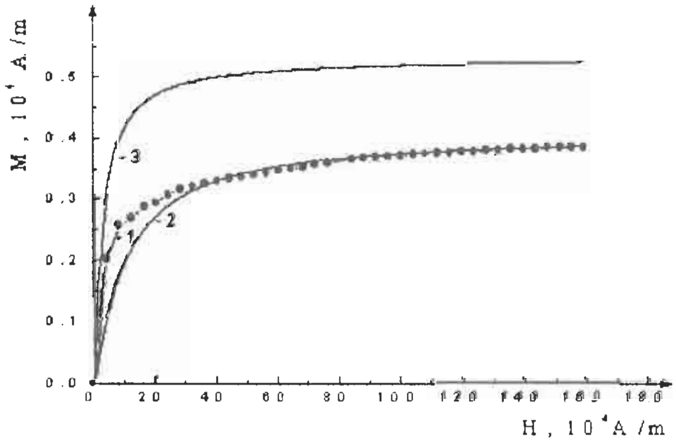

Fig.1b Magnetisation curves of sample III (b) at $\varphi_s = 0.007$ obtained experimental (curve 1), by Langeven equation without and with take into account non-magnetite layer (curves 2, 3).

which has been solved at following conditions: a) $x = const$, that is non-magnetite layer equally in all nanoparticles and independent its size; b) $d_g = const$, system is monodisperse and in this case must $x = const$; c) $x = d_g \cdot k$, non-magnetite layer is linear function of geometrical size of nanoparticles.

At take account these conditions equation (1) transformed to

a) $$x^3 - 3\cdot\overline{d_g}x^2 + 3\cdot\overline{d_g^2}x - (1-\alpha)\overline{d_g^3} = 0 \qquad (1a)$$

б) $x^3 - 3\cdot d_g x^2 + 3\cdot d_g^2 x - (1-\alpha)d_g^3 = 0$ (1б)

c) $(k-1)^3 + \alpha = 0$ (1c)

Values of α are 0.606, 0.556, 0.509, 0.381 correspondingly for samples I, II, III and IV. Values of $\overline{d_g}, \overline{d_g^2}, \overline{d_g^3}$, taked from [4] (see table 1a). Thickness of non-magnetite layer determined from equations 1(a), 1(b), 1(c) and values of "*k*"for samples I, II, III and IV are presented in the columns (a), (b), (c) and (d) of the table 1(b), respectively. Analysis of obtained results and take into account conditions of preparation of these samples [6-8] showed, that value of non-magnetite layer increase by increasing of nanoparticles size and also depended from properties of carrying mediums (columns I(b), I(c) of table 1(b)). This is described, that quantity of molecule absorbed to surface of nanoparticles is increased with increasing size of nanoparticles and is changed in dependence of properties of carring mediums. Agreement of average values of non-magnetite layer and its near to parameter of crystal cell of massive magnetite (0.839 nm) indicate, that reaction of formation non-magnetite layer in magnetic nanoparticles occurs by diffusion mechanism.

Table 1. a) Values of $\overline{d_g}$, $\overline{d_g^2}$, $\overline{d_g^3}$ and of sample I, II, III, IV; b) Values of non-magnetite layer and value "k", obtained from equations 1(a), 1(b), 1(c).

a)

Samples	$\overline{d_g}$, nm	$\overline{d_g^2}$, nm^2	$\overline{d_g^3}$, nm^3
I	9.48	95.46	1020.04
II	7.76	65.49	600.484
III	7.33	56.65	460.949
IV	5.44	30.94	183.867

б)

Samples	(a) x, нм	(b) x, нм	1(c) x, нм	1(d), k
I	0.83	0.728	0.729	0.154
II	0.83	0.689	0.689	0.178
III	0.83	0.738	0.739	0.201
IV	0.83	0.809	0.747	0.275

Kaiser R. and Miskolzy G. have described one of reason of formation of non-magnetite layer in [9] and Bibik E.E. and et.al [10]. Decreasing of contains magnetic substance in probability is related with chemical demagnetisation of surface of magnetite nanoparticles, the interaction of molecule of surface active stabilizer with magnetite nanoparticles consequently formation of non-magnetite salt - oleat iron, which is non-magnetite layer.

2.1. Kinetic equation of description of mechanism of formation of non-magnetite layer.

Changing of concentration of reagent *(C(r,t))* in time may be is described by following diffusion equation

$$\frac{\partial C(r,t)}{\partial t} = D\nabla^2 C(r,t) - KC(r,t) \quad (2)$$

where D- the diffusion coefficient, K – the reaction constant.

Use dimensionless value $x=r/r_0$ in equation (2), where r_0 is source radius of nanoparticles and after transform to spherical coordinate system we obtain

$$\frac{\partial C(x,t)}{\partial t}=\frac{D}{r_o^2}\frac{\partial^2 C(x,t)}{\partial^2 x}+\frac{2D}{r_0^2 x}\frac{C(x,t)}{\partial x}-KC(x,t) \tag{2'}$$

Solution of equation (2') will be to find as production of two functions $C(x,t)=A(x)\cdot B(t)$ [11] at following boundary condition $C(x,t)|_{t\to 0}=0$, $C(x,t)|_{t\to\infty}=C_0$. After substitute this to equation (2') we obtain two equations, solution of second equation is $B(t)=(1-e^{-\lambda t})$ and first equation is become:

$$D\frac{1}{r_0^2}\frac{1}{A(x)}\frac{\partial^2 A(x)}{\partial x^2}+\frac{2D}{r_0^2}\frac{1}{x}-\frac{\partial A(z)}{dx}\frac{1}{A(x)}-K=-\lambda \tag{3}$$

We obtain Rikatti type equation [12] after consequently introducing new variables $U(x)$ by transformation $A'(x)=U(x)\cdot A(x)$ and $V(x)$ by $V(x)=U(x)+\frac{1}{x}$ in equation (3)

$$V'(x)+V^2(x)-\gamma r_0^2=0 \tag{4}$$

where $\gamma=\frac{\lambda-K}{D}$.

Solution of equation (4) is:

$$V(x)=\sqrt{\gamma}r_0 th(\sqrt{\gamma}xr_0)$$

After back transformation obtain

$$A(x)=\frac{const}{x}cth(\gamma xr_0+C_0\gamma r_0)$$

Dependence of thickness of non-magnetite layer from time is:

$$\frac{3}{r}\rho\frac{dr(t)}{dt}=KCe^{-\lambda t}const\frac{1}{x}cth(\sqrt{\gamma}r_0+C_0\sqrt{\gamma}r_0)$$

ρ is density of bulk magnetite (5.24 g/m^3) and $\frac{dr(t)}{dt}=r_0\frac{dx}{dt}$

Then definitively expression of thickness of non-magnetite layer is:

$$r(t)=r_0[\ln[tg[\frac{KC_0}{6\rho\lambda}(1-e^{-\lambda t})\gamma r_0+\frac{\pi}{4}]]] \tag{5}$$

Value of non-magnetite layer and rate of change in asymptotic is:

$$r(t)|_{t\to 0}=0,\qquad r(t)|_{t\to\infty}=\frac{1}{3}\frac{KC_0}{\rho\lambda}\sqrt{\gamma}r_0,\qquad \left.\frac{dr(t)}{dt}\right|_{t\to 0}=\frac{1}{3}\gamma^{3/2}\frac{KC_0}{\rho}r_0,$$

$$\left.\frac{dr(t)}{dt}\right|_{t\to\infty}=0$$

3. NUMERICAL CALCULATION

As see from (6) r(t) at initial time is equal to zero and future exponentially is increase and at big time is plateau. Change of thickness of non-magnetite layer from time at initial time is maximum, at big time it practically is stopped.

Numerical analysis of expression (5) of non-magnetite layer has been carried out at value C_0= 1kg/m^3 , K_1 = 51.519·10^{-14}, K_2 = 26.828·10^{-14}, K_3 = 73.628·10^{-14}, K_4 = 55.26·10^{-14}, K_i constant of reaction magnetite with *NaOH, 2% SDS, H_2O, NH_3OH* correspondingly, which was been used for precisation, washing, stabilzation of magnetite nanoparticles. Value of K_i was been calculated by formule in [13].

Program on the base of (5) has been written in FORTRAN algorithmic language and realized in PENTIUM computer.

4. RESULTS AND DISCUSSION

Typical curves of formation non-magnetite layer in dependence time in take into account size of magnetite nanoparticles are presented in fig.2. Analysis showed, that saturation of formation non-magnetite layer is reach in during 8-10 minutes and depended from size of nanoparticles and properties of carrying mediums.

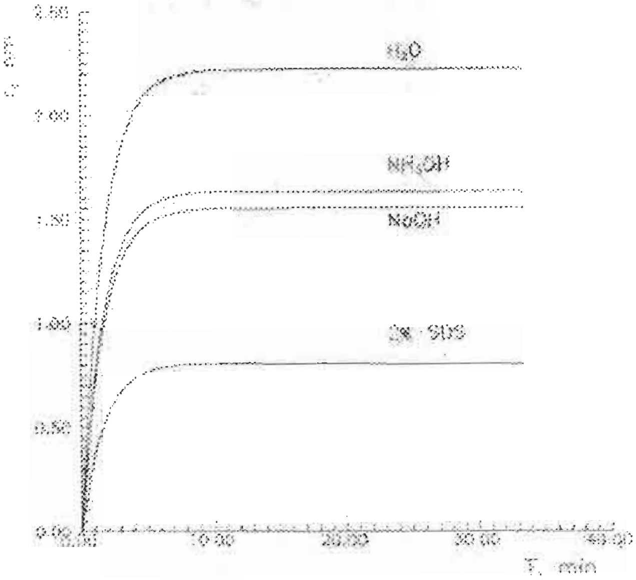

Fig.2 The dependence of formation non-magnetite layer in sample I from preparation time of nanoparticles at presence *NaOH*, NH_3OH, H_2O, *2% SDS*.

In fig.3 are presented the dependence of value of thickness of non-magnetite layer from molecular weight carrying medium. As see with decreasing of molecular weight of reagent increased of saturation time.

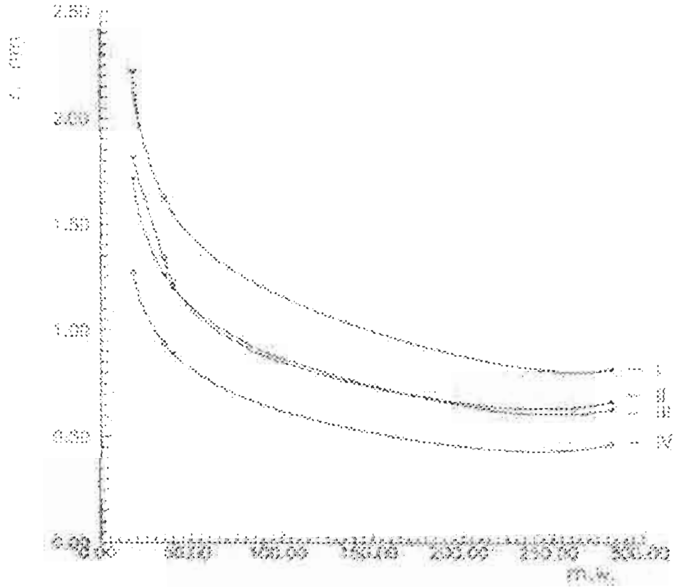

Fig.3 The dependence of formation non-magnetite layer in samples **I**, II, III and **IV** from molecular weight of reagents.

In fig.4 are presented the dependence of formation of non-magnetite layer from time at presence of NH_3 for samples I, II, III and IV.

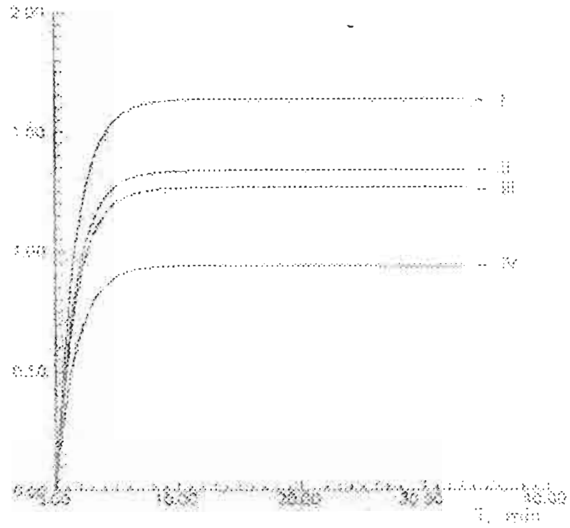

Fig.4 The dependence of formation of non-magnetite layer in samples I, II, III and IV at presence NH_3OH

Results of linear regression analysis ***($r = A + Br_0$)*** of thickness of non-magnetite layer from reacted reagents H_2O, $NaOH$, NH_3OH, *2% SDS* at different size of nanoparticles are: (A,B): (-0.061, 0.085), (-0.224, 0.164), (-0.128, 0.173) and (-0.899, 0.234), respectively. Take into account, that in all cases value of A more less in comparing value B, we will be suggested, that non-magnetite layer may be describe by $r = Br_0$. Comparing of value of k (from table 1) and value of B we obtain, that "k_I"corresponded to B_I (index i corresponded to order of samples), that in reality characterised method of preparation of samples.

Results of linear regression analysis of dependence of non-magnetite layer from size of nanoparticles in different reagents are: $(A, B) = (0.624 \cdot 10^{-3}, 0.234)$; $(-0.164 \cdot 10^{-2}, 0.164)$; $(-0.107 \cdot 10^{-3}, 0.173)$; $(-0.225 \cdot 10^{-3}, 0.085)$ correspondingly for H_2O, $NaOH$, NH_3OH, *2% SDS*. As see with increasing molecular weight of reagents value of non-magnetite layer is decreased.

Investigation of distribution of magnetite nanoparticles on non-magnetite layer showed, that it is like to distribution of nanoparticles on size and allow use distribution nanoparticles on size to characterisation of non-magnetite layer (average value, dispersity and etc.). This is suggested by theorem in [14]. Parameters of distribution nondimensional data are: $\bar{x}=0.385$, $\sigma=0.423$, $\gamma= 0.687$, $\varepsilon = 0.451$, $p_k =1.741$.

Thus, take into account above indicating may be suggested that, non-magnetite layer is formated in magnetite nanoparticles at its synthesis. Mechanism of formation of non-magnetite layer is diffusion of molecule arround medium to nanoparticles, saturation of formation of non-magnetite layer is reach at during 8-10 minutes. Value of non-magnetite layer depended from of size and conditions of preparation of magnetite nanoparticles. Non-magnetite layers prevent future oxidation of magnetite nanoparticles. Non-magnetite layer is significant with decreasing diameter of nanoparticles for which, magnetization saturation of samples is decreased strongly.

[1] *Bibik E.E., Matigullin B.Ya., Raycher Yu.L., Shliomis M.I.* Magnitnaya gidrodinamika, 1973, v.1, P.68.

[2] *Kaiser R., Miskolczy G.* Journal of Applied Physics, 1970, v. 41, N. 3, P.1064

[3] *Ali-zade R.A., Lukin Yu.V., Mayorov M.M., Plyavinsh Yu.A., Buryakov A.N., Lauva M.T., Turkin S.I., Blum E.Ya., Zubov V.P.* Tez.dokl. XII Rijskoy konferensii po magnitnoy gidtodinamike, 1987, P.91.

[4] *Ali-zade R.A., Buryakov A.N., Lukin Yu.V., Zubov V.P.* Tez.dokl.Vsesoyznoy konferensii po magnitnim jidkostyam, Moskva, 1988, V.1, P.4

[5] *Ali-zade R.A.* Phys B(Proc.Suppl) 1998, v.63, P.406

[6] *Buryakov A.N., Grichkova I.A., Zubov B.P., Lukin Yu.V., Turkin S.I., Donchak V.A., Fedorov V.A.* Sposob polucheniya magnetonapolnyennich polimerov. A.S. 1628478, Rossia, USSR

[7] *Turkin S.I., Lukin Yu.V., Markvicheva E.A., Ali-zade R.A., Zubov V.P., Zavalniy M.A., Skuinsh A.G., Kyavinsh M.K., Zichmanis A.H.* Sposob polucheniya jelatinovich micronositeley. A.S. N 1486515, Rossia, USSR

[8] *Turkin S.I., Lukin Yu.V., Markvicheva E.A., Ali-zade R.A., Zubov V.P., Zavalniy M.A., Skuinsh A.G., Kyavinsh M.K., Zichmanis A.H.* Sposob polucheniya magnitnich micronositeley. A.S. N 1567623, Rossia, USSR

[9] *Tichonov A.N., Samarski A.A* Uravneniya matematicheskoy fiziki. M.: Nauka, 1977, S.736.

[10] *Stepanov V.V.* Kurs differentialnich uravneniy. M.: Gosudarstvennoye Izd.-vo Fiz.-mat. literaturi, 1959, S.468.

[11] *Eyring G., Lin S.G.* Osnovi chimicheskoy kinetiki. Perevod s anglitskogo pod.red.d-ra chim.nauk, prof. A.M.Brodskogo. Moskva, Izd.-vo Mir 1983, S.528.

[12] *Khudson D.* Statistika dlya fizikov. Perevod pod red. E.M.Leikina M.; Mir 1970, S.296.

NANOMAQNETIT ZƏRRƏCIKLƏRIN KIMYƏVI SUSPENZIYA METODU ILƏ ALINMASI ZAMANI ONLARIN SƏTHINDƏ QEYRI MAQNETIT MADDƏNIN ƏMƏLƏ ĞƏLMƏ KINETIKASI.

RASİM Ə. ƏLİ-ZADƏ

Nanomqnetit zərrəciklərin 2 və 3 valentli dəmir duzlarının birgə məlulunun ifrat ölcüdə qələvi ilə suspenziya edilməsi ilə alınması zamanı onların səthində qeyri maqnetitin maddənin əmələ gəlməsi təsdiq olunmuşdur. Qeyri maqnetit maddənin əmələ gəlmə mexanizmi, onun qalınlığının nanomaqnetitin ölçülərindən və alınma şəraitindən asılılığı tədqiq olunmuşdur.

КИНЕТИКА ФОРМИРОВАНИЯ НЕМАГНЕТИТНОГО СЛОЯ НА ПОВЕРХНОСТИ НАНОЧАСТИЦ МАГНЕТИТА ПРИ ПРИГОТОВЛЕНИИ ИХ МЕТОДОМ ХИМИЧЕСКОГО ОСАЖДЕНИЯ

РАСИМ А. АЛИ-ЗАДЕ

Было установлено существование немагнетитного слоя на поверхности наночастиц магнетита полученного химическим осаждением 2 и 3 валентных солей железа в избыточной щелочи. Был исследован механизм формирования немагнетитного слоя на поверхности наночастиц магнетита, зависимость толщины немагнетитного слоя от размера и условий подготовки магнетита.