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KINETICS OF THE FORMATION OF AMORPHOUS Nd-Fe-B PARTICLES BY CHEMICAL REDUCTION

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Abstract - Fine and ultrafine Nd-Fe-B particles have been obtained from metallic cation reduction by borohydride ions both in water and microemulsions. In this way amorphous particles of different sizes ranging from 4-50 nm to 100-400 nm can be obtained. In this work we will report on the kinetics of the growth of the particles studied by stopped-flow with UV-Vis detection. Quantum effects are suggested for the particles with sizes about 5 nm.

1- INTRODUCTION

Magnetic materials are widely used in modern technology. They are fundamental elements in areas such as information, telecommunications and electronic devices. The development of magnetic materials conditions in a decisive way the advance in these areas. In particular, important advances in these fields are related with the investigation and development of films and magnetic particles /1/.

Even though the study of ultrafine particles is known since the beginning of colloidal chemistry, introduced by the English chemist Thomas Graham in 1861, the interest for fine and ultrafine magnetic particles has not taken hold until the last few years in which the technology demanded materials of higher performance and smaller sizes /2/.

For the preparation of magnetic particles of amorphous alloys there are, fundamentally four basic procedures /3/:

- rapid quenching
- deposition of atoms in vaporized state
- solid state reaction
- chemical reactions in solution.

Among the methods we mention, the rapid quenching method is the most widely used. This method consists in rapidly cooling the fused material (see figure 1). This restricts the production of alloys to those with a composition which is close to the eutectic point (E).

On the other hand, with the chemical method it is possible to obtain alloys with any composition within the interval corresponding to the temperature at which the chemical reaction is carried out, and what is more important, it permits the direct production of fine and ultrafine particles with sizes smaller than $\cong 0.1 \mu\text{m}$ /4/. Particles of 1 - 10 nm are easily obtained with this procedure.

Recently an original method was developed by the authors /5-7/ for obtaining fine and ultrafine Nd-Fe-B particles of controlled size. In this work we present a preliminary study of the formation kinetics for the

magnetic particles in different experimental conditions.

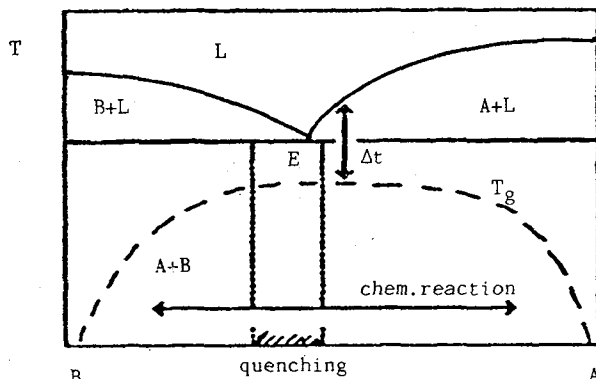


Fig. 1 - Phase diagram of a simple AB system. E = eutectic point. T_g = glass temperature. Compositions of metallic glasses which can be obtained by rapid quenching and chemical reactions are shown.

2- EXPERIMENTAL PROCEDURE

The following procedure was developed for obtaining the magnetic particles of Nd-Fe-B. A solution with an adequate ratio of the metallic cations Fe^{2+} and Nd^{3+} was mixed with another of borohydride. There were two ways of mixing the solution, one was the dropwise addition of the reduction agent solution onto the one with the metallic ions and the other was by rapidly and directly mixing them using of a "tee-junction". This way, we obtained fine particles with different ratios Nd/Fe/B and with sizes between 100 and 400 nm /7/. In order to control the growth of the particles we carried out the reaction in the presence of microemulsions /5/. In this case, we mixed two identical microemulsions, one containing the reduction agent and the other the metallic salts. We found that the real size of the particles ($\cong 4 - 50$ nm) was determined by the size of the droplets which made up the microemulsion. In this work the microemulsions we used were "water-in-oil" microemulsions composed of heptane/water/aerosol-OT (sodium bis-(2-ethyl, hexyl) sulphosuccinate) with a concentration of 0.05M in aerosol-OT (AOT) and different ratios $R = [H_2O]/[AOT]$. For this type of microemulsions the size of the water droplets may be calculated to a first approximation using the equation: r (radius of the droplet)/nm = $0.175 R + 1.5$ /8/.

The composition of the samples obtained was studied by chemical analysis, ICP (induced coupled plasma) and X-ray fluorescence.

The structure was determined by the X-ray diffraction technique (CuK_{α} radiation) observing that the particles obtained were in the amorphous phase. After exposing these particles to thermal treatments in an Ar atmosphere, they evolved to the crystalline state.

The kinetic experiments were performed with a combination of a stopped-flow developed in our laboratory and a diode array spectrophotometer (HP 8452A).

The basic magnetic properties of the samples obtained were measured with a SQUID magnetometer in the $2 < T(K) < 300$ temperature range. The magnetic materials are soft and they present, at room temperature, values for the coercivity field of $H_c = 170$ Oe and for the saturation magnetization of $I_s = 60$ emu/g.

3- EXPERIMENTAL RESULTS

In order to understand the mechanism for the formation of these magnetic particles we have carried out different types of studies.

3.1- Static measurements

In the first place, we performed experiences by means of UV-Vis spectrophotometry in the wavelength range $200 < \lambda(\text{nm}) < 500$. According to the sizes of the particles we mention before, we can differentiate three behaviors depending on the size/wavelength ratio a/λ . In figure 2 we represent these three regions:

- 1) Rayleigh region: $a/\lambda \ll 1$ (a =radius of an spherical particle).
- 2) Mie region: $a/\lambda \approx 1$
- 3) Optical region: $a/\lambda \gg 1$.

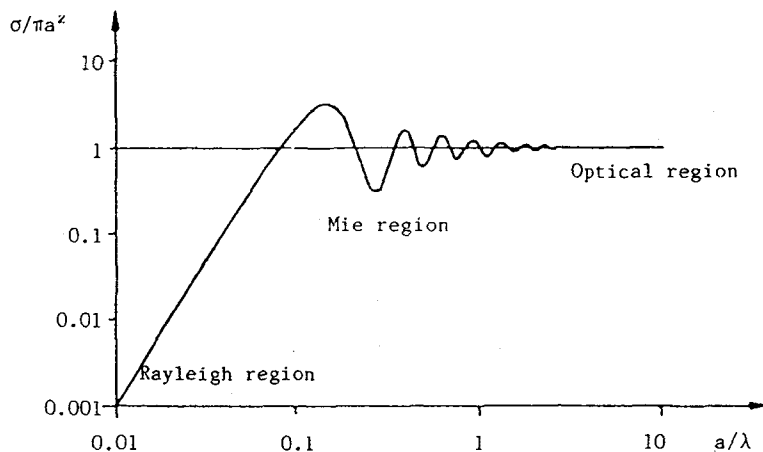


Fig. 2 - Effective cross-section (σ) of an spherical particle. a = radius of the particle. λ = wavelength.

Therefore, for the particles obtained in water ($a \cong 100-400$ nm) we must expect a Mie behavior from the spectrophotometric observation. In figure 3 we clearly observe a continuous drop in the absorbance superimposed with resonances of the Mie type. For particles which are smaller than these wavelengths, such as those obtained in microemulsions ($a/\lambda < 1$) we can expect a monotonous drop in the absorbance (Rayleigh region) due to the fact that the effective cross-section of the particles decreases.

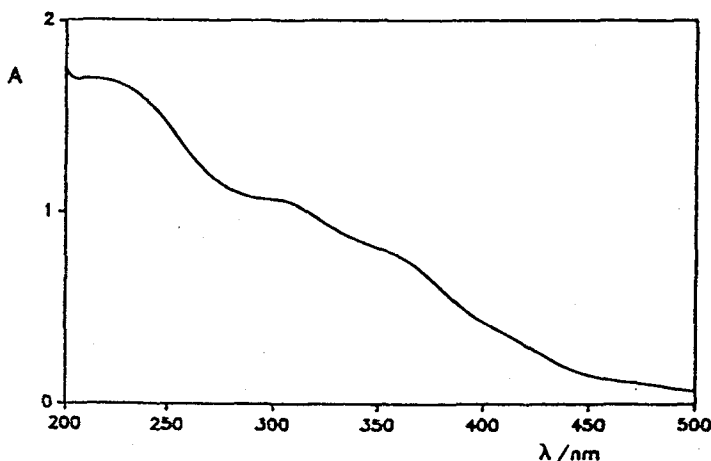


Fig. 3- Absorption spectrum of colloidal NdFeB obtained in water showing the existence of Mie resonances.

In figure 4 we present a characteristic spectrum obtained for the ultrafine particles. As it can be seen, the behavior is not of the Rayleigh type and two maxima appear in this interval of wavelengths which can be attributed to the existence of quantum effects due to the small size of the particles. These effects, which have been found in other semiconducting ultrafine particles [12-16], is associated by most authors to the separation of the energy levels in the conducting band of the semiconductor due to the small dimensions of the particles. Because of this they are called Q-particles. According to this interpretation, the quantum effects should disappear when we increase the size of the particles. This is so, in figure 5 we can observe for particles of sizes around 15 nm this effect disappears and we only observe the continuous band corresponding to the electronic absorption of this semiconducting material.

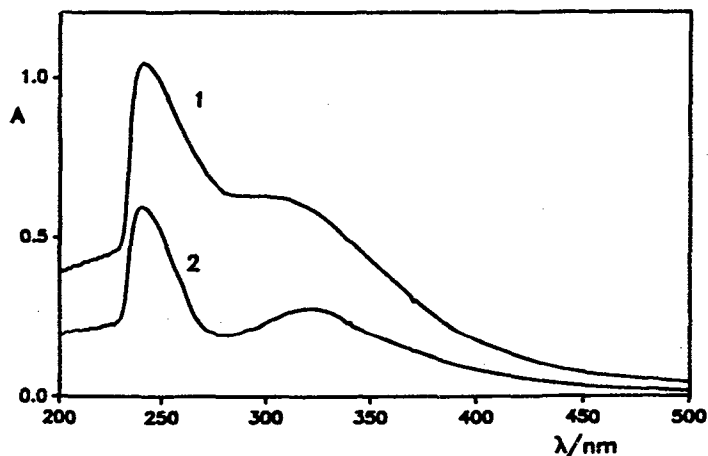


Fig. 4- Absorption spectra of colloidal NdFeB obtained in microemulsions ($R = 13$) showing the presence of quantization effects.

1) $[\text{FeCl}_2] = 1.14 \times 10^{-3} \text{ M}$; $[\text{NdCl}_3] = 2.22 \times 10^{-4} \text{ M}$; $[\text{NaBH}_4] = 5.28 \times 10^{-3} \text{ M}$.
 2) Concentrations reduced by a factor 6.

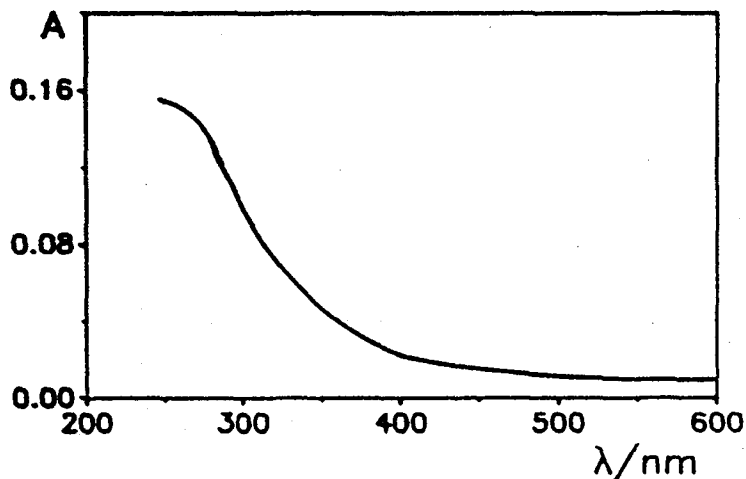


Fig. 5- Absorption spectrum of colloidal NdFeB obtained in microemulsions with $R = 30$ ($r_{\text{droplet}} \cong 6.5 \text{ nm}$) showing the classical electronic absorption. $[\text{FeCl}_2] = [\text{NdCl}_3] = 1.5 \times 10^{-4} \text{ M}$; $[\text{NaBH}_4] = 7.6 \times 10^{-4} \text{ M}$.

It is also necessary to point out in this section that there exists a small dependence of the final size of the particles obtained in microemulsions with the concentration of reactives used. As an example, we show in figure 6 the variation of the UV-Vis spectra with the concentration of the reactives. According with the above discussion the results clearly reflect the increase in size of the particles with the concentration.

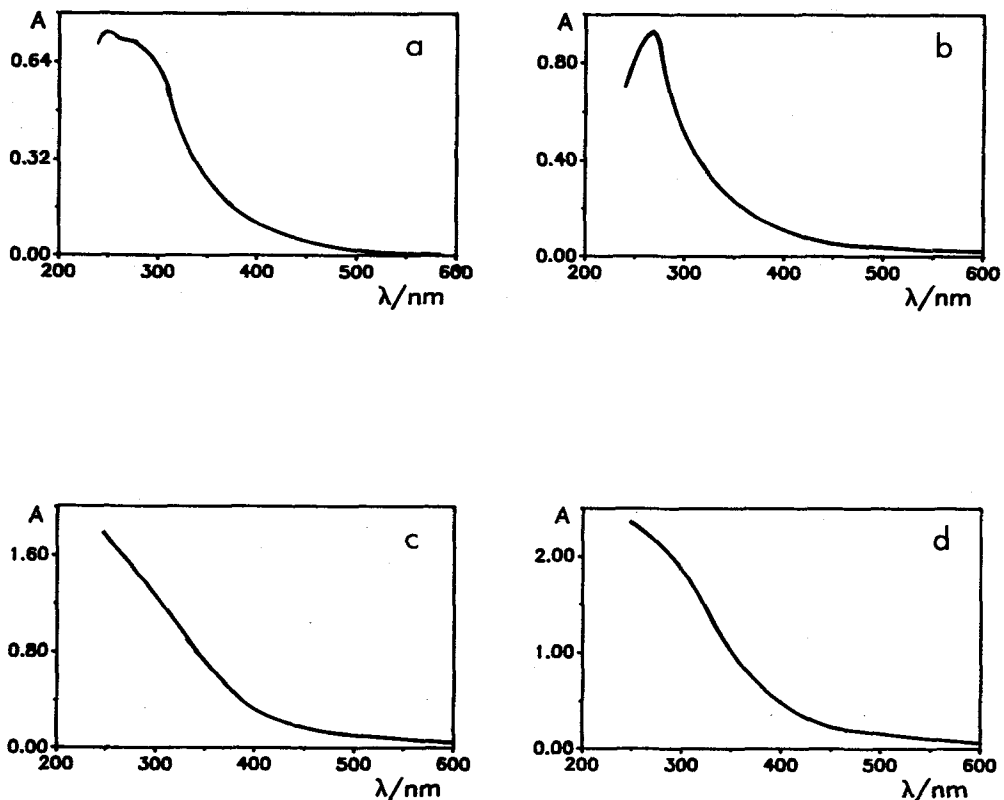
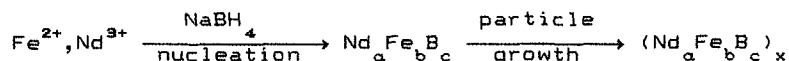


Fig. 6- Absorption spectra of colloidal NdFeB obtained in microemulsions ($R = 22$) showing the increase in the particle size with the reactant concentrations. $[\text{FeCl}_2]/[\text{NdCl}_3]/[\text{NaBH}_4]$: a) 1.9/0.37/8.8; b) 2.7/2.7/13.6; c) 8.2/2.7/25; d) 13.6/2.8/36.0 ($\times 10^{-3}\text{M}$).

3.2- Kinetic measurements

Figure 7 and figure 8 show the UV-Vis absorption spectra during the formation of the particles in microemulsions and water respectively.

We have systematically observed in all the experiments performed that the shape of the curves and the positions of the maxima do not vary with time during the formation of the particles. This seems to indicate that within the mechanism that can be used to explain the formation of the particles (see scheme 1), the limiting step is the chemical reaction faster for the formation of the nuclei and that the final growth of these is faster.



Scheme 1- Proposed mechanism for the formation of colloidal NdFeB.

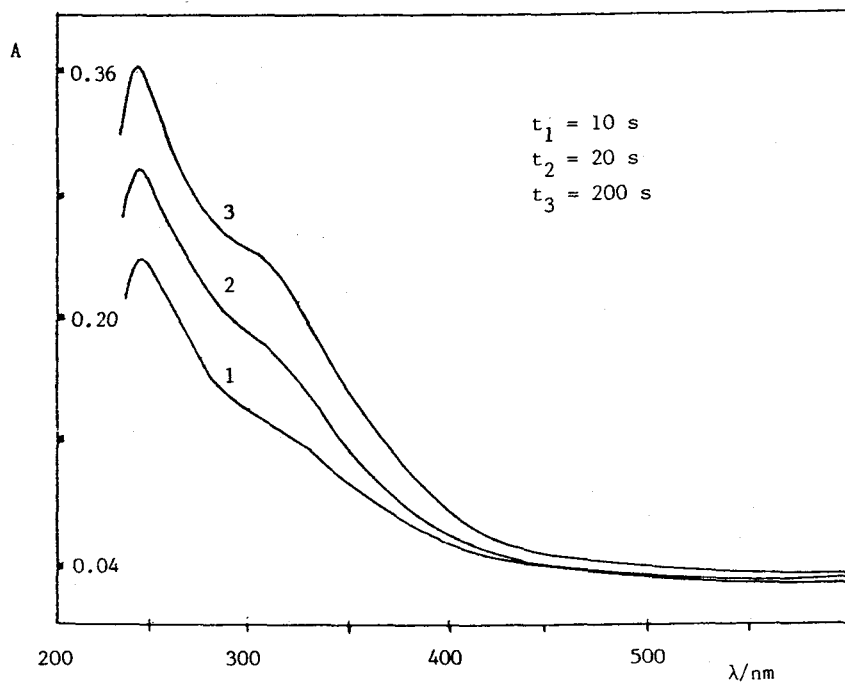


Fig. 7-Time-resolved absorption spectra of colloidal NdFeB obtained in microemulsions ($R = 10$). $[\text{FeCl}_2] = 8.6 \times 10^{-5} \text{ M}$; $[\text{NdCl}_3] = 1.7 \times 10^{-5} \text{ M}$; $[\text{NaBH}_4] = 3.9 \times 10^{-4} \text{ M}$.

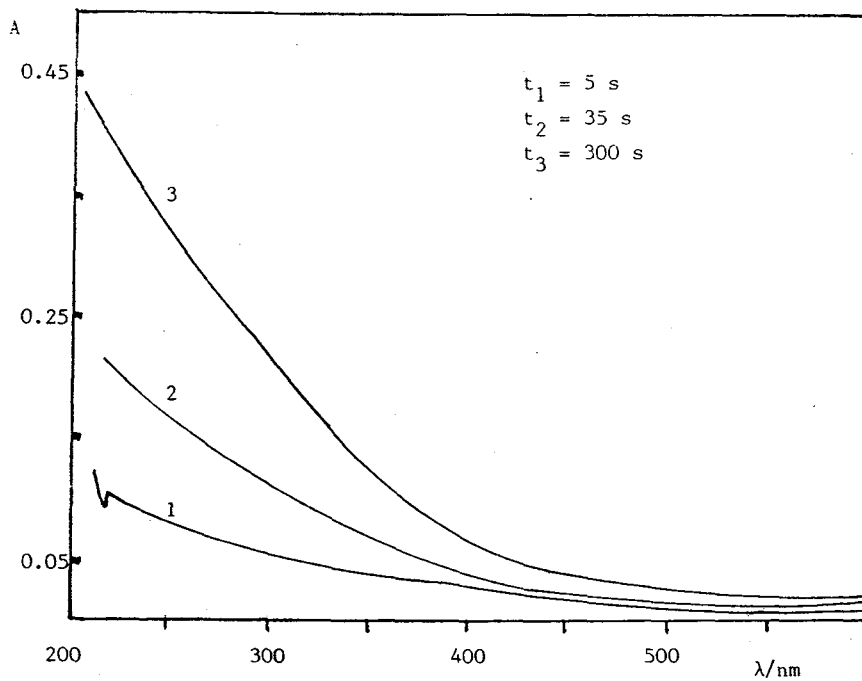


Fig. 8- Time-resolved absorption spectra of colloidal NdFeB obtained in aqueous solution. $[\text{FeCl}_2] = [\text{NdCl}_3] = 1.5 \times 10^{-4} \text{ M}$; $[\text{NaBH}_4] = 7.6 \times 10^{-4} \text{ M}$.

We have also studied the magnetic a.c. susceptibility during the formation of the particles /6/ and performed preliminary measurements of time-resolved small-angle X-ray scattering by synchrotron radiation (DESY, Hamburg, FRG). All of these results seem to support the mechanism here proposed.

From the experimental results here reported we can then conclude:

- 1) The existence of quantum effects in ultrafine NdFeB particles and
- 2) The formation of colloidal NdFeB seems to take place by a chemical reaction and nucleation which are much slower than the growth of the nuclei.

Finally, we must point out that these are preliminary results and that more experiments are at the moment being carried out (synchrotron, time-resolved neutron scattering, etc.) in order to clarify the mechanism of the formation of colloidal NdFeB.

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