Patterns of aggregation in coprecipitation reactions

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Prismatic polycrystalline magnetic particles of iron oxalate were grown by allowing the aggregation of the precipitating crystallites that were produced by a reaction between aqueous iron salts and oxalic acid solutions. The experiments were done at room temperature and under different pH conditions. The particle-growing process was followed by optical microscopy and was then digitally recorded. The effect of the presence of a static magnetic field on the coprecipitation process was also analyzed. It was found that both pH and applied field, considerably influence the aggregation of the crystallites. This is clearly shown in the mean size and surface quality of the particles. It was observed that high pH values produce larger particles and that the applied field yields particles with a smoother surface than those obtained without the application of the field. The polycrystalline particles grow with the formation of clusters whose spatial distribution can be characterized by scaling relations. From this scaling behavior, some information about the spatial correlations occurring during precipitation can be obtained.

Keywords: Magnetic materials; aggregation in crystal growth.

Se crecieron partículas magnéticas prismáticas policristalinas de oxalato de hierro permitiendo la agregación de cristalitos precipitados que fueron producidos por una reacción entre soluciones acuosas de sales de hierro y ácido oxálico. Los experimentos se realizaron a temperatura ambiente y bajo diferentes condiciones de pH. El proceso de crecimiento de las partículas fue seguido por microscopia óptica y digitalmente grabado. El efecto de la presencia de un campo magnético estático en el proceso de agregación también fue analizado. Se encontró que ambos, el pH y el campo magnético, influyen considerablemente en la agregación de los cristalitos. Esto se muestra claramente en el tamaño medio y la lisura de la superficie de los cristalitos. Se observó que para altos valores de pH se producen partículas mayores y que el campo magnético aplicado produce partículas con superficie más lisa que aquellas crecidas sin la aplicación del campo. Las partículas policristalinas crecen con la formación de clusters cuya distribución espacial puede ser caracterizada bajo relaciones de escalamiento. Del comportamiento de este escalamiento es posible obtener alguna información sobre las correlaciones espaciales que ocurren durante la coprecipitación.

Descriptores: Materiales magnéticos; agregación en el crecimiento cristalino.

PACS: 75.50.-y; 81.10.-h; 07.60.Pb

1. Introduction

Soft processing methods to obtain inorganic materials have attracted a growing interest in the materials chemistry community because of the increasing demand for environment friendly approaches to the synthesizing of advanced materials [1,2]. Soft solution methods such as precipitation, coprecipitation, and thermohydrolysis are examples of these. Their uses have been discussed exhaustively in the literature [3-6].

Despite of their popularity as easy-handling procedures, from the microscopic point of view the coprecipitation methods in fact involve very complex phenomena, including, at different stages, simultaneous nucleation, thermally-activated transport, non-steady aggregation, coarsening, etc. The detailed time evolution driven by the reactions is still not well understood, as has been recently discussed [7].

Although the aggregation of the crystallites is the final stage in the process of coprecipitation, its analysis can provide some insights into the previous stages and can help to better understand different aspects of the kinetics of the reaction, which influences the final morphology of the polycrystalline particles. Many condensed matter systems are produced by aggregation processes, and the relationship of these processes to the interactions governing them are currently a subject of interest in many fields of research. This is the case

because, to some extent, the features of the pattern formation determine the physical-chemistry properties of the systems.

Despite their diversity, the common characteristic of possessing a fractal structure has been found in several types of complex systems generated by the aggregation of particles.

In the presence of applied fields, it was shown that their structure exhibits multifractal characteristics in rheological fluids, and under certain conditions this can be associated with the existence of various stages of the aggregation process. The physical properties of the clusters formed during these stages determine some of the macroscopic physical properties of those complex fluids. In this sense, it was shown that the sound propagation modes in magneto-rheological fluids can be calculated from the elastic properties of some of those clusters [8]. Based on this fractal cluster structure, the changes measured in the thermal diffusivity, induced by different intensities of an applied electric field, was explained in the electro-rheological fluids [9].

Most of the crystal growth studies concerning the aggregation processes have mainly focused on understanding the phenomena related to solution growth methods. In this study, particular attention has been paid to the role of the solid-liquid interfaces in the crystal growth processes and there have been several reports regarding the aggregation processes, for example, in biomineralization phenomena that oc-

cur in the production of aggregates of calcium oxalate mono-hydrate [10]. One of the purposes of those investigations was to understand the role of the concentration of the various urinary species and of the pH conditions in determining the morphology of the polycrystalline aggregates produced [11,12].

In this study, we discuss our measurements and observations of the spatial patterns formed by the polycrystalline particles which were grown by the aggregation of crystallites generated by the coprecipitation reactions of aqueous solutions of iron (III) nitrate, iron (II) chloride, ammonium oxalate, and oxalic acid at room temperature. This reaction was studied under various pH conditions. The effect of an applied static magnetic field during the complete reaction process was also analyzed. By this procedure, micrometric-sized polycrystalline particles with prismatic morphology were always obtained. The size of the particles and the quality of their surface were affected by the pH value at which the reaction develops as well as the applied field.

2. Experimental

The reaction of aqueous solutions of iron (III) nitrate, iron (II) chloride, ammonium oxalate, and oxalic acid, produces iron oxalate nanometric crystallites that precipitate, and then these crystallites aggregate to form micrometric polycrystalline particles. Their polycrystalline character was corroborated by polarized optical microscopy between crossed polars. The preparation was discussed in detail in Ref. 16. These iron oxalate particles were used as a precursor in the synthesis of magnetite particles. The coprecipitation reaction is as follows:

$$FeCl_{2(aq)} + 2Fe(NO_3)_{3(aq)} + (NH_4)_2C_2O_{4(aq)}$$
$$+ 3H_2C_2O_{4(aq)} \rightarrow FeC_2O_{4(s)}$$
$$+ Fe_2(C_2O_4)_{3(aq)} + 2NH_4Cl_{(aq)} + 6HNO_{3(aq)}$$
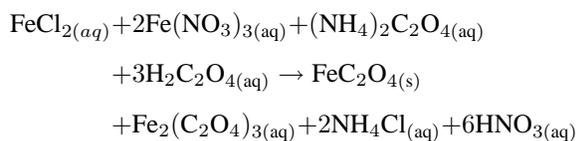
where (aq) = aqueous solution and (s) = solid

To avoid the formation of the undesirable hydroxides, such as $Fe(OH)_2$ and $Fe(OH)_3$, from iron ions in solution, it is important to maintain the pH value of the medium below 6, because it has been observed that the formation of these hydroxides are favored at higher pH values [14,15].

Some information regarding the coprecipitation reaction and the process of aggregation of crystallites can be obtained by observing the characteristics of the resulting polycrystalline particles and by studying the clusters that they form.

To directly observe these processes, an optical stereomicroscope was used in the transmission mode. All studies were carried out in a cell made up of a Teflon rectangular frame and limited by glass walls made up of standard microscope slides. The cell size was 14mm×65mm×5mm. The formation of the clusters by the polycrystalline particles was recorded by a digital video camera. From this camera, digital pictures were taken at different stages to study the patterns in the spatial
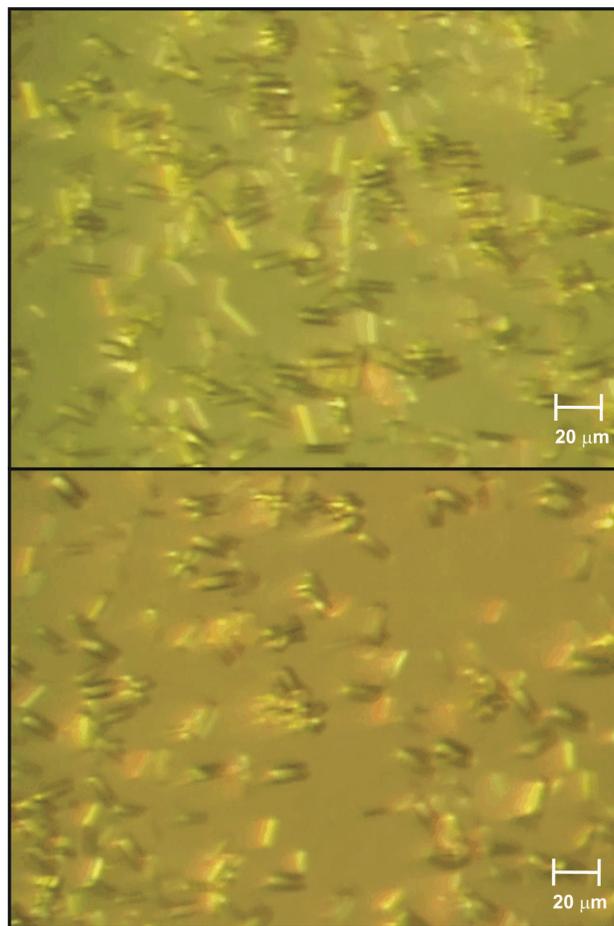
FIGURE 1. Microphotographs of the distribution of particles of iron oxalate at the end of the coprecipitation reaction. pH =1.2 upper and 5.4 lower.

distribution and to evaluate the spatial correlations. The coprecipitation reactions were performed at several pH values. Here, only two of them are discussed, at pH = 1.2 and 5.4, which are representative of low and high pH conditions, respectively. By adding a buffer solution of acetic acid, the pH value was controlled and the formation of iron hydroxides was avoided. The static magnetic field (H = 0.022T) was applied by a permanent magnet.

To observe the morphology, size, and surface smoothness of the resulting polycrystalline particles, scanning electron microcopy (SEM) studies were performed using a JSM 5400 LV (Jeol) system.

3. Results and discussion

Figure 1 shows microphotographs of the distribution of polycrystalline particles as they grow in the bottom of the cell. These are produced by the aggregation of the precipitating crystallites resulting from the reaction, (upper) pH = 1.2 and (lower) pH = 5.4. This is the situation at the end of the precipitation process. No magnetic field was applied. The distribution of these polycrystalline particles in clusters is a
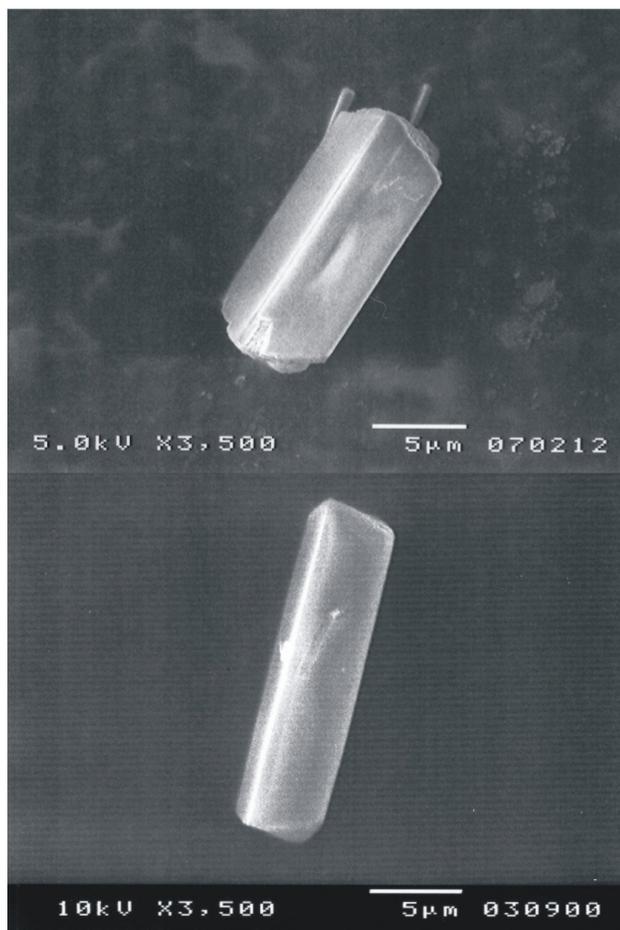
FIGURE 2. SEM micrographs of prismatic polycrystalline particles of iron oxalate obtained by aggregation of crystallites during a precipitation process, for two different pH values, upper pH =1.2 and lower pH =5.4.

manifestation of the complex correlations, which influence the precipitation of crystallites.

SEM micrographs of typical single polycrystalline particles for both pH values, 1.2 upper, and 5.4 lower, appear in Fig. 2. The comparison of these pictures makes it clear that the pH condition at which the chemical reaction occurs affects the surface smoothness and the size of the particles.

We wish to investigate if there is some relationship between the size and surface smoothness of the particles and the form in which the particles are distributed in clusters on the cell bottom. Finally, a trial to characterize the complexity of the cluster structure formed by the polycrystalline particles can be performed. Some of these typical distributions are shown in Fig. 1. It was found that by a multifractal analysis performed on these structures during the processes of pattern formation, the spatial correlations existing in these structures can be revealed. In this manner, the pattern complexity can be characterized and to some extent quantified. In this analysis, the mass fractal dimension of the cluster structure was measured on digital pictures. The mass fractal dimension is defined by the power law: $m \sim r^D$ where m is the mass contained in a circle of gyration radius r. If this scaling relation fits well in the measurements, then the exponent D, with a value in the interval $1 < D < 2$, is called the mass fractal dimension. This approach has been used to study several diverse complex systems and the mass fractal dimension has proven to be a useful tool to characterize a great diversity of two-dimensional structures. In particular, it has been used to investigate the complex structures in rheological suspensions generated by the application of external fields [8,16].

To evaluate D on the digital images of the distributions of clusters of polycrystalline particles, it is necessary first to make a high-contrast treatment of the images to define a single plane in the structure. Afterwards, we numerically draw a number of equally separated concentric circles, starting with a circle with a diameter of the order of the mean size of the polycrystalline particles, up to circles as large as the observation field permits, with the separation between contiguous circles also of the order of the polycrystalline particles mean size. If, in a given element of area, the number of pixels, N, spanned by the particles is proportional to the mass contained in that element of area, the distribution of mass may be evaluated as a function of the gyration radius. This procedure was repeated by randomly selecting different sites as centers of the set of circles in the photograph. To avoid the effects of small local inhomogeneities and to mainly capture the trends and correlations of the global structure statistically, the average of the number of pixels obtained was calculated for the corresponding circles for all sites in the structure. Empirically it was found that taking ten sites and sets of thirty circles is enough to obtain statistically consistent results.

Figure 3 shows the graph of $\log_{10} N$ vs $\log_{10} r$ measured on the final structure of clusters, which was formed by the coprecipitation processes, corresponding to pH = 1.2 and 5.4.
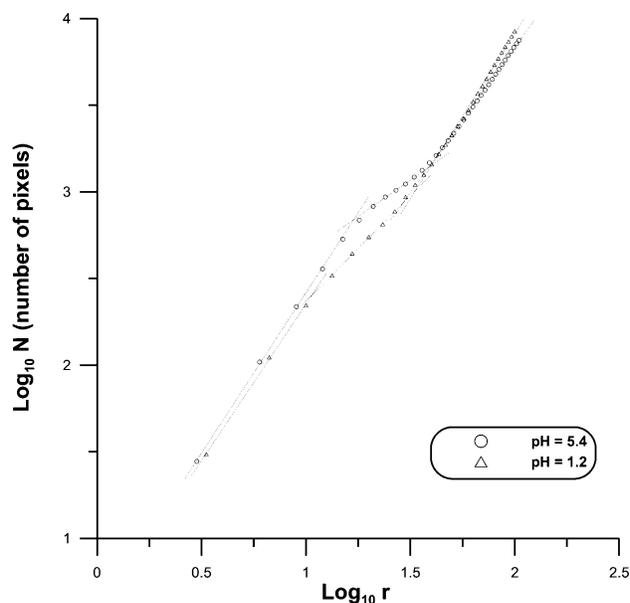
FIGURE 3. $\log_{10} N$ vs $\log_{10} r$ for the final structures formed by the polycrystalline particles obtained by the coprecipitation process at different pH conditions. The values of r are expressed in terms of the particle mean size σ.
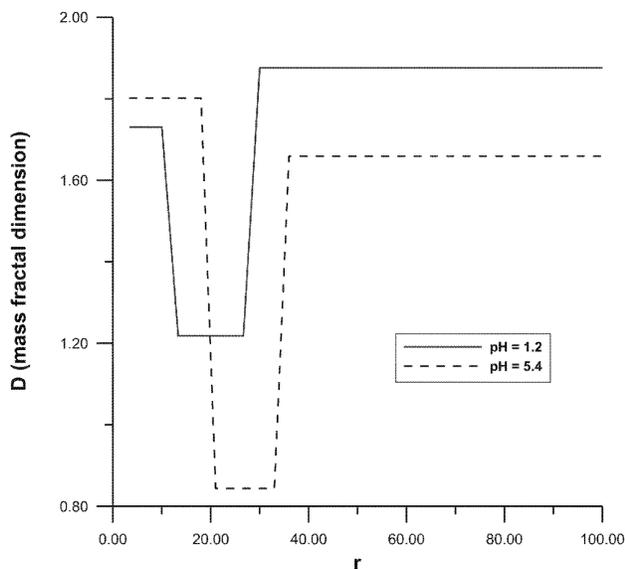
FIGURE 4. The mass fractal dimension D as a function of r for the values pH = 1.2 and 5.4 respectively.

N_i is the average number of pixels contained in the circle of radius r_i. In both graphs, it can be observed as various straight segments. These segments might be associated with different correlations, which can be described by scaling relations in the clusters of polycrystalline particles. In Fig. 3, a straight line has been fitted to each straight segment using a least squares procedure. The slope of each straight line would be the mass fractal dimension of the structure, corresponding to that range of r values.

Thus, the structure of the aggregates reveals multifractal characteristics.

Obviously, there should be a complex correlation of these fractal characteristics with the conditions under which the coprecipitation reaction develops, for instance, concentration of the reagents, pH value, temperature, etc. Qualitatively one may understand why the pH value affects the correlations observed in the various scaling intervals shown in Fig. 3. Considering that the presence of protons in the solution affects the kinetics of the reactions, which in turn determines the growth and precipitation rates of the crystallites. The process, when briefly described, would be as follows: when the size of first crystallites generated by the reaction becomes large enough to overcome the thermal agitation, the precipitation process begins. These particles reach the bottom of the cell and grow continuously as a result of the aggregation of new precipitating crystallites, which are deposited on them. This later stage is influenced by a weak magnetic interaction. Obviously, the magnetic nature of this interaction is due to the presence of the iron ions. As a result of this aggregation, polycrystalline particles grow until the reaction is completed. It is expected that the flatness of the surface and the size of the polycrystalline particles would be determined by the size of the crystallites and the rate at which these crystallites precipitate. In this regard, it is reasonable to expect that a constant low precipitation rate for the small crystallites makes it more likely to obtain a better smoothness of the particle surface when compared with any other conditions.

When the precipitation reaction terminates, some of the characteristics of the clusters of prismatic polycrystalline particles like such as their mass fractal dimension and the range of the correlations described by the scaling exponents can be quantified. The changes in the scaling exponents is noticeable; however, from the logarithmic graph, plotted in Fig. 3, it is not easy to obtain a quantitative appreciation of the magnitude of slope variation. Thus, in Fig. 4 the graph of the value of the mass fractal dimension was directly shown as a function of the radius belonging to Fig. 3. It should be noticed that the ranges of r, corresponding to each definite value of the mass fractal dimension, could be associated with an average size of the substructures formed by the clusters observed in Fig. 1. In other words, the pH conditions of the coprecipitation reaction affect the distribution of the polycrystalline microparticles in a complex way, as is shown in the different D values. By comparing the first D values for both pH values, it was observed that, although the particle mean size is similar, the mean size of the smallest aggregates is around 70μm for pH = 1.2 and the size is double for pH = 5.4, whereas for the second and third largest range of correlation of the aggregates, the most noticeable feature is not the change in mean size but the differences in the D value itself.

The general trends observed in this process of aggregation of oxalate crystallites, namely, the formation of aggregates exhibiting spatial correlations of various ranges, could be the general pattern for various types of precipitates. For instance, similar patterns of aggregation were observed during the coprecipitation of calcium silicates obtained by the reaction of aqueous solutions of calcium chloride dyhydrate (2M) and sodium silicate pentahydrate (0.2M), according to the reaction:

$$Na_2SiO_3 \cdot 5H_2O_{(aq)} + 2CaCl_2 \cdot 2H_2O_{(aq)}$$
$$\rightarrow Ca_2SiO_{4(s)} + 2NaCl_{(aq)} + 2HCl_{(aq)} + 8H_2O,$$
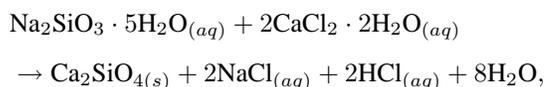
where (aq) = aqueous and (s) = solid.

To gain some insight into the significance of the magnetic interaction, especially in determining the surface smoothness of the iron oxalate particles, this coprecipitation process was studied at pH = 5.4 in the presence of an applied static magnetic field (H = 0.022T).

Figure 5 shows photographs of the distribution of microcrystals produced by the coprecipitation reaction in the presence of a magnetic field H = 0.022T applied during the entire process. On the right hand side, the corresponding graph of $\log_{10}N$ vs $\log_{10} r$ taken at the beginning (a), a middle stage (b), and the final stage (c) of the process is shown. By comparing the distributions shown in Fig. 1, it can be observed that in the presence of applied field there appears to be some orientational order. Figure 5a shows an early stage of the growing microparticles as observed with the stereomicroscope. While the coprecipitation reaction occurs, these microparticles along with the other particles will continue to
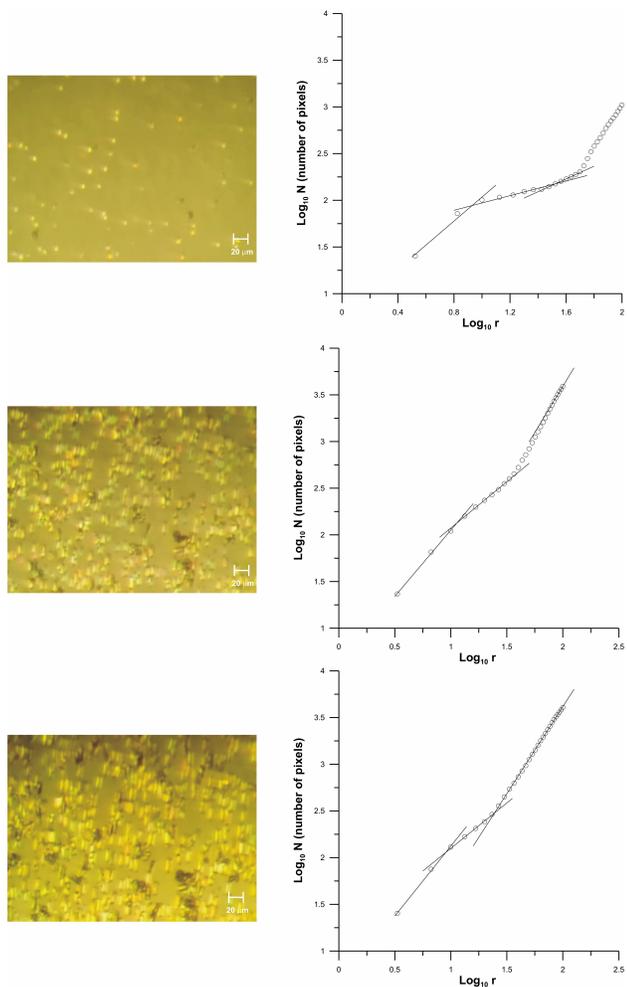
FIGURE 5. Microparticles distribution during the coprecipitation process at pH =5.4 and with an applied static magnetic field (H = 0.022T). The photographs show the beginning (upper), a middle stage and the final of the process (lower). The corresponding graph of $\log_{10}N$ vs $\log_{10}r$ is shown next in the right.

attract crystallites. The graph $\log_{10}N$ vs $\log_{10}r$ corresponding to this distribution appears next to the right in the figure. Although in the figure only few particles are seen, the total distribution shows some definite scaling trends indicating that in the distribution there are some spatial correlations. However, in the last portion of the curve it is not possible to associate a scaling relation. Of course, under these conditions at several portions of the curve it is inappropriate to evaluate a properly defined mass fractal dimension. This is so not only due to the lack of a well defined slope but due to the small range of r values in which a scaling relation could be associated. As expected, this deficiency is more notorious at the earlier stages of the aggregation. In Fig. 5b one observes small clusters formed by some few particles and other larger agglomerates. This is quantified by means of their scaling relations, which can be obtained from the graph $\log_{10}N$ vs $\log_{10}r$. In this graph it is evident that the distribution of microparticles is formed by aggregates of three different mean sizes. In addition to this mean size, each one of these type of
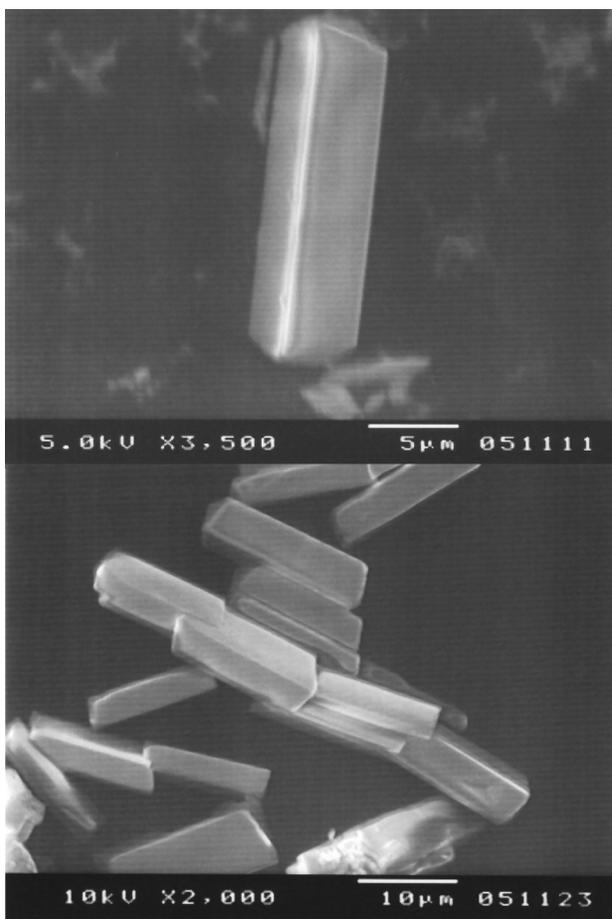
FIGURE 6. SEM micrographs of a single particle and a first-order agglomerate of polycrystalline particles. These were produced guided by an applied magnetic field.
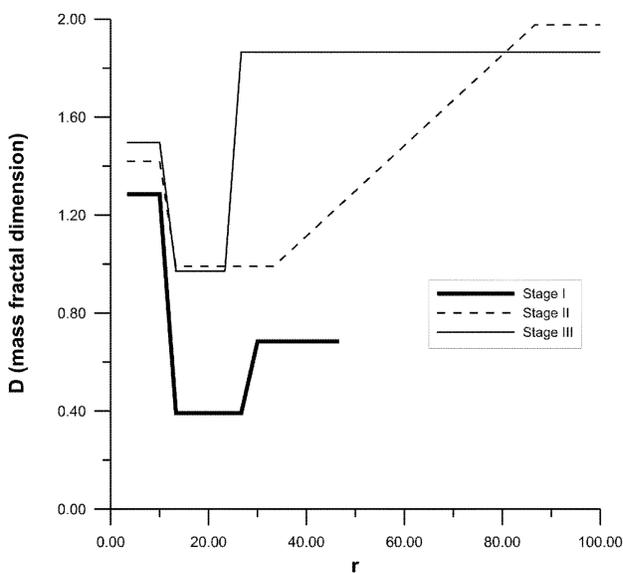
FIGURE 7. The mass fractal dimension D as a function of r at different stages of the coprecipitation process with a magnetic field H = 0.022T . In the intervals of r values where the curve is inclined there is not possible associate a scaling relation.

substructures is also characterized by its scaling exponent; in this case it is better defined than in the previous situation. In the last stage of the coprecipitation process, as shown in Fig. 5c, the trends described for Fig. 5b reach their final condition. There are some quantitative differences in the mean size of the sub-structures; however, the qualitative behavior of the curves remains the same.

Figure 6 shows SEM micrographs of (a) a typical first-order agglomerate of polycrystalline particles, with a size around 70μm, and (b) a single particle. They were grown in the presence of a static magnetic field (0.022T) at pH = 5.4. It is evident in the SEM micrographs that the surface smoothness is improved when the coprecipitation process develops in the presence of a static magnetic field.

For the conditions discussed above, the size distribution of the particles is sharp around 20μm. The agglomerate shown in Fig. 6a exhibits an incipient average orientation of the particles in the direction of the applied field. The single particle shown in Fig. 6b exhibits a smoother surface than those prepared without the application of the magnetic field.

Figure 7 shows the behavior of the scaling exponent, D, as a function of the radial distance r, for the distribution of polycrystalline particles shown in Fig. 5. Attention should be paid only to those intervals in which the scaling relation is well defined and those intervals where the curve appears inclined are not considered. It was observed that the mean size of the smallest agglomerates is almost similar at the different stages of the coprecipitation process, being around 70μm, whereas the mean size of the second generation agglomerates changes considerably during the process. This is shorter at the end of the process than in the initial stages. It was observed that this behavior appears only when the coprecipitation is made in the presence of the applied field. It indicates that the sub-structures associated with the largest agglomerates get even longer in the presence of the field, thus reducing the mean size of the medium-sized agglomerates.

It may be concluded from this that these dynamical modifications of the correlations expressed in these scaling relations become possible because of the orientational order imposed by the applied field.

4. Conclusions

Iron oxalate crystallites were obtained by coprecipitation reactions of aqueous solutions. The aggregation of these crystallites produces micrometric polycrystalline particles. This process was studied under several conditions of pH and applied magnetic field. Generally, the structure of these agglomerates reveals multifractal characteristics. The pH value at which the coprecipitation reaction develops, influences the distribution of aggregates and the morphology of the particles in a complex way.

The existence of these spatial correlations can be quantified by scaling relations, and can be associated with different mean sizes of agglomerates of the polycrystalline particles. It was found that at pH = 5.4 a better surface smoothness of the micrometric polycrystalline particles are obtained in comparison to that prepared at pH = 1.2. If additionally the coprecipitation reaction is performed in the presence of an applied magnetic field, the process of aggregation of the crystallites can be to some extent guided, improving the particles surface smoothness. The agglomerates of polycrystalline particles generated in these conditions show some orientation parallel to the applied field and its spatial distribution also exhibits multifractal characteristics.

Acknowledgments

1. M. Yoshimura and J. Livage, *MRS Bull.* **25**(2000) 12.

2. M. Yoshimura, W.L. Suchanek, and K. Byrappa, *MRS Bull.* **25** (2000) 17.

3. J. Livage, M. Henry, and J.P. Jolivet in: L. Henchard and J.K. West (Eds), *Chemical processing of advanced materials* (John Wiley & Sons, New York, 1992).

4. E. Matijevic, in: L. Henchard, and J.K. West (Eds), *Chemical processing of Advanced Materials* (John Wiley & Sons, New York, 1992).

5. N. Kosai, H. Mitamura, H. Fukuyama, F. Esaka, and S. Komarneni, *J. Mat. Res.* **20** (2005) 2997.

6. A.A. Athawale and M. Bapat, *J. Metastable and Nanocrystalline Materials* **23** (2005) 3.

7. B.L. Cushing, V.L. Kolesnichenko, and C.J. O'Connor, *Chem. Rev.* **104** (2004) 3893.

8. J.L. Carrillo, F. Donado, and M.E. Mendoza, *Phys. Rev. E.* **68**(2003) 0615091.

9. F. Donado, M.E. Mendoza, V. Dossetti, E. López-Cruz, and J.L. Carrillo, *Ferroelectrics* **270**(2002) 93.

10. M. Asta, F. Spaepen, and J.F. van der Veen, *MRS Bull.* **29** (2004) 920.

11. A.A. Chernov, J.J. De Yoreo, L.N. Rashkovich, and P.G. Vekilov, *MRS Bull.* **29** (2004) 927.

12. D.T. Wu, L. Granasy, and F. Spaepen, *MRS Bull.* **29** (2004) 945.

13. K.G. Christmas, L.B. Gower, S.R. Khan, and H. El-Shall, *J. Colloid Interface Sci.* **256** (2002) 168.

14. S.R. Qiu, *et al.*, *Proc.Natl.Acad.Sci*. **101**(2004) 1811.

15. C. Domingo, R. Rodriguez-Clemente, and M. Blesa, *J. Colloid Interface Sci.* **165** (1994) 244.

16. M.E. Mendoza, F. Donado, R. Silva, M.A. Pérez, and J.L. Carrillo, *J. Phys. Chem. Solids* **66** (2005) 927.