SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE MAGNESIUM OXIDE

Jamaleddin Esalah, Hounida S.Omar, Haifa Ben Zekri, and Ramzi Hader*

Department of Materials & Metallurgical Engineering,
Al-Fateh University, Tripoli, Libya

*General Water Authority, Tripoli, Libya

الملخص

تم تحضير مسحوق متناهي الدقة (نانومتري) لأكسيد الماغنيسيوم عن طريق تفاعل (ترسيب) كيميائي بين أكسيد الليثيوم المتميء ونترات الماغنيسيوم وقد تمت دراسة تأثير كل من درجة الحرارة وسرعة التحريك وكذلك درجة إحلال وطريقة إضافة أحد المواد المتفاعلة على حجم حبيبات المسحوق المتكونة.كما تم توصيف المسحوق باستخدام حيود الأشعة السينية (X-ray diffraction) والمسح الإلكتروني المجهري (SEM). القياسات أثبتت أن حجم حبيبات المسحوق المتحصل عليه هو ما بين 18 إلى 36 نانومتر.

وجد أن درجة الحرارة لها تأثير على حجم الحبيبات وأن الحجم يتناقص بزيادة درجة الحرارة. كما تبين أن سرعة التحريك ودرجة إحلال أحد المواد المتفاعلة وطريقة إضافتها إلى المادة المتفاعلة الأخرى ليس لهما تأثير على حجم الحبيبات.

ABSTRACT

Magnesium oxide nano-powder is synthesized by precipitation from colloidal solutions by the chemical reaction approach using $LiO.H_2O$ and $MgNO_3$. The effects of temperature, stirring speed, dilution and addition method on the grain size of the produced magnesium oxide powder have been investigated.

The powder was characterized using the X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The XRD and SEM measurements indicate that the magnesium oxide powder produced by the chemical technique has a crystal structure size in a range of 18-36 nanometers.

The results obtained through out the course work of experimental runs conducted showed no significant effect of stirring speed, dilution and method of addition on the particle size, while variation of temperature was found to have a little effect on the particle size.

KEYWORDS: Nano-particles; Nano-powder; Nanocrystalline; Magnesium oxide; Chemical precipitation;

INTRODUCTION

Nanocrystalline materials refer to those materials with grain sizes less than 100nm. In general, nanocrystalline materials are a subset of "nanostructured" materials, which include all materials intentionally constructed with one or more dimensions in the nanometer range [1]. The motivation for manufacturing and studying nanocrystalline materials lies in the unique properties they possess. As the grain size becomes smaller and smaller, a large and larger fraction of atoms resides on the grain boundaries.

In the early of 1980s, the German researchers were the first to produce materials with a grain size in the nanometer range [1]. The gas condensation method was the candidate method for the production of materials with grain sizes typically less than 100 nm. Since that time other synthesis techniques have been developed. Over the last two decades, inert gas condensation [2.3], amorphous precursor processing [4,5], electrochemical processing [6], laser deposition [7], sputter deposition [8], electron beam vapor deposition [9], and sol-gel processing [8,9] techniques have been successfully used to produce nanocrystalline materials.

As might be expected, there are advantages and disadvantages of each of the powder nanosized materials synthesis approaches. The chemical techniques can produce chemically pure powders [10]. A large knowledge base of chemical thermodynamic and kinetic theory is also available to aid in manipulating such reactions. In many cases, the chemical reactions used for the preparation of nanocrystalline powder are quite simple and old in origin, for example, the burning (oxidation) of magnesium and zinc has long been known to produce nanocrystals of MgO and nanofibrils of ZnO, respectively, since these were confirmed at an early stage by the existence of transmission electron microscope (TEM) [11].

The chemical methods also have their disadvantages. One disadvantage is that the surfaces of chemically produced particles tend to be contaminated by adsorbates from the medium in which they are produced. Perhaps the more serious concern is that the chemical approach is not a general one. For each new composition desired in nanocrystalline powder form, a new reaction with different starting chemicals, reaction kinetics, and relationships between reaction conditions and powder characteristics must be identified and optimized [10].

Nanocrystalline materials represent a novel class of materials with grain sizes less than 100 nm resulting in significant increases in grain boundaries and triple junction volume [4].

Many of the studies showed strong agreement with the notion that grain boundaries in nanocrystalline materials are not unlike those in polycrystalline materials. Notably, the grain boundary within nanocrystalline materials was observed to be approximately 1nm, which corresponds well with what had been observed previously in polycrystalline materials [6]. The primary difference between polycrystalline materials and nanocrystalline materials is the increase in the volume fractions of grain boundaries and triple junctions in the latter. This intercrystalline volume fraction has been quantified by Palumbo et al. using three dimensional treatment involving tetrakaidecahedral grains [8].

The main reason that the nanocrystalline materials have their own unique properties is the large intercrystalline volume fraction that is present in these materials. Techniques such as x-ray diffraction [12], extended x-ray absorption fine structure (EXAFS) [13], hydrogen absorption [14] and self-diffusivity [15] have shown that the interfacial component in nanocrystalline materials forms a distinct microstructural constituent. The intercrystalline area consists of arrays of atoms with a certain degree of disorder in comparison to those found in the grain interior. The exact structure of the grain boundaries in nanocrystalline materials is still unknown. Observations by Wunderlich et al. [9] on interfaces using High Resolution Electron Microscopy (HREM) showed an "extended" structure for the grain boundaries in nanocrystalline material which is not typically observed at the grain boundaries in conventional materials. On the

other hand, Thomas et al. [16] observed that the interfacial structure of nanocrystalline material is consistent with that typically observed in coarse-grained materials.

Palumbo et al. [17] have put forward a model where the grain shape is represented by a regular fourteen sided tetrakaidecahedron. The faces of the tetrakaidecahedron represent grain boundaries and the edges represent the triple junctions. A triple junction is defined as the intersection line of the adjoining crystals. By considering the grain size to be represented by the maximum diameter (d) of an inscribed sphere, the intercrystalline volume fraction can be calculated.

The microstructure of nanocrystalline materials is different from the structures of amorphous and crystalline materials, and as a result of this difference the properties of nanocrystalline materials are expected to be different from the properties of chemically identical substances in the amorphous and crystalline state. It should be noted that many of the early studies on nanocrystalline materials were conducted on materials produced by gas condensation and many of these results disagree with more recent measurements on nanomaterials produced by other methods. Nowadays, in most production techniques there are still tremendous difficulties in producing nanocrystalline materials in a form that can be mechanically tested using traditional testing methods. This is necessary to obtain mechanical data, which can be compared directly to data for the normal crystalline solid for the same material.

The design of technological materials used in industry depends on the availability of raw material with outstanding properties in terms of composition, purity, size and size distribution. Different techniques have been tried to produce nano-sized oxide powders. Magnesium oxide is one of the important materials which, is used as a catalyst, in toxic waste remediation, as additives in, paints and superconductor products, especially when it is used in the nano-sized scale.

In this study, the approach of wet chemical method is used to prepare the nano-size particle of MgO where the synthesis parameters: temperature, stirring speed, addition method and concentration of solutions are controlled. The magnesium oxide powder nanophase is synthesized from precipitation from colloid solutions by the chemical reaction approach using $LiO.H_2O$ and $MgNO_3$ and characterized using the X-ray diffraction and Scanning Electron Microscopy.

EXPERIMENTAL WORK
Materials
Magnesium Nitrate (Mg $(NO_3)_2.6H_2O$) with a purity of 99% and Lithium Hydroxide ($LiOH.H_2O$) with a purity 98% were used in this work. The chemicals are supplied by the department of chemistry / Al-Fateh University, and used without further purification. The distilled water is supplied by Libyan Petroleum Institute.

A solution with a concentration of 0.01M was prepared by dissolving 5.18g of Mg $(NO_3)_2.6H_2O$ in distilled water of total volume of two liters. Lithium Hydroxide with a concentration of 0.02 M was prepared by dissolving 1.71 g of Li OH $.H_2O$ in distilled water of total volume of two liters.

Experimental Procedure
Magnesium Hydroxide precipitate was formed by adding 300ml of magnesium nitrate solution with a concentration of 0.01 M to a 300 ml of Lithium Hydroxide solution with a concentration of 0.02 M. The effect of dilution was investigated by the addition of 300 ml and 600ml of water to the 300 ml of 0.01 M magnesium nitrate solution. All solutions were prepared with distilled water.

$$2 \text{ LiOH.H}_2\text{O} + \text{Mg(NO}_3)_2.6\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + 2\text{LiNO}_3 + 8\text{H}_2\text{O}$$
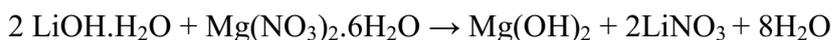
The samples were stirred in tightly closed flasks at specific stirring rates and then left to reach equilibrium. At equilibrium, a white fine precipitate was formed. The two phases were separated by centrifuging the samples in (centrifuge) for 30min at 3000 rpm, and then filtrated using fine grain round filter papers.

Magnesium Hydroxide precipitates were prepared at different experimental conditions. The effects of temperature, dilution, addition method, and stirring speed on the characteristics of the precipitate were investigated.
After separation, the precipitates were heat treated in an oven at 600°C, through which, the precipitate was converted to magnesium oxide according to the reaction:
$$\text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$$
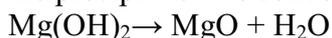
Characterization

X-ray diffraction was used to identify the precipitates as well as, to estimate the particle size of the product. In addition, scanning electron microscope (SEM) was used to study powder morphology and the type of agglomeration.
For the XRD experiments, the samples were loaded onto cell provided with the spectrometer (X-Ray diffract meter (D5OO5). The crystallite size of a powder sample can be estimated from the X-ray broadening by using the well-known Scherrer equation [18,19]:
$$B(2\,\theta) = 0.89\,\lambda / L \cos\theta$$
Where B(2 θ) is the width of the X-ray pattern line at half peak-height in radians, λ is the wave length of the X-ray (1.540 A° for the Cu Kα_2), θ is the angle between incident and diffracted beams in degrees, and L is the crystallite size of the powder samples in angstroms. The contact time to the atmospheric environment was kept to minimum (about 2-3 minutes). The spectrometer was set at 40 kV and 45 mA and typical scans were from 3 to 110.25 (2θ) at 0.033/min.

The hydrated MgO sample was held onto a small piece of sticky transparent tape on top of the specimen mount stub for the electron microscopy study. For the heat-treated (dehydrated) sample, the sample loading was carried out inside a N_2 bag and was kept in plastic box inside desiccators during the period before the gold-coating operation. A gold film of about 30 nm thickness was obtained from a sputtering coater with four layers of 10-s coating time. The SEM pictures were taken by using Auto scan Model Spectrometer.

RESULTS AND DISCUSSION

Several nano-MgO samples with different particle sizes were obtained using the different experimental conditions. As shown in Figure (1), both the intensities of the reflections in the XRD pattern and their FWHM (full width at half maximum) varied with the experimental condition. All the prepared samples were calcined at 600 ^{o}C. The powder prepared was investigated using the X-ray diffraction technique and the Scanning Electron Microscopy. The results showed that the powder particle size was in the range of nano-size particles (18 – 36 nm).

The powder samples prepared were investigated using X-ray diffraction technique (XRD) and Scanning Electron Microscopy (SEM). Figure (1) shows a representative sample of the XRD results obtained. Both the intensities of the reflections in the XRD pattern and their full width at half maximum (FWHM) varied with the experimental

condition, indicating that there are different particle sizes. The results showed that the powder particle size was in the range of nano-size.
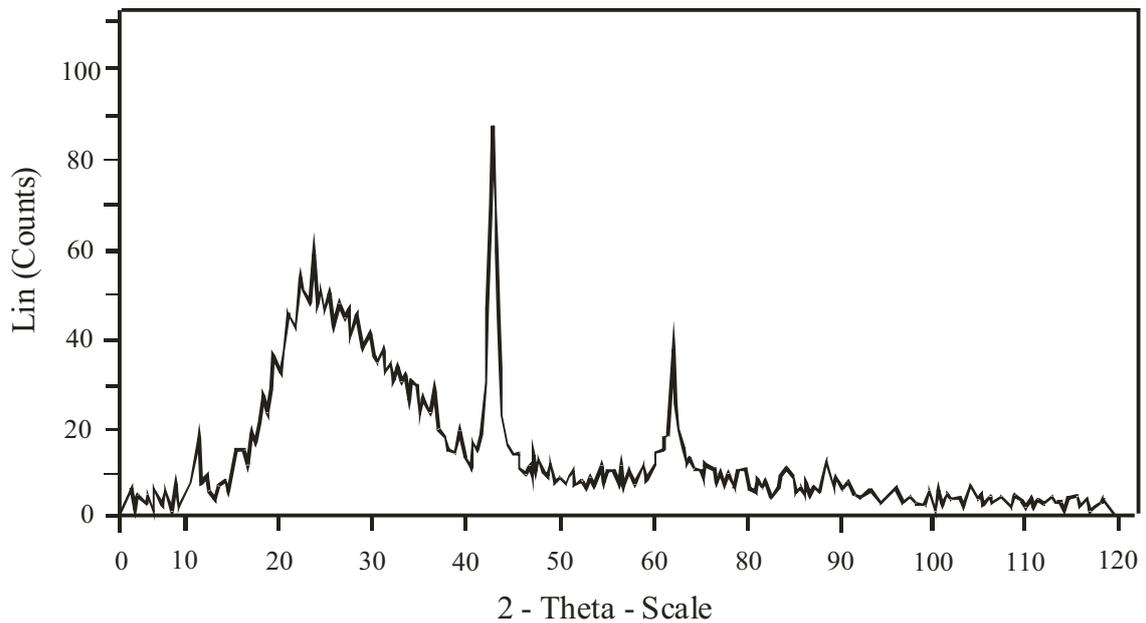

Figure 1: X-ray diffraction chart for the experimental conditions: 300 ml, 250 t/min, one portion, RT, 10 min

Representative images of the SEM are shown in Figures (2 – 4). The micrographs shown in these figures are taken under different magnification to illustrate the cluster packing density and the particle size of the produced particles by the different experimental conditions.
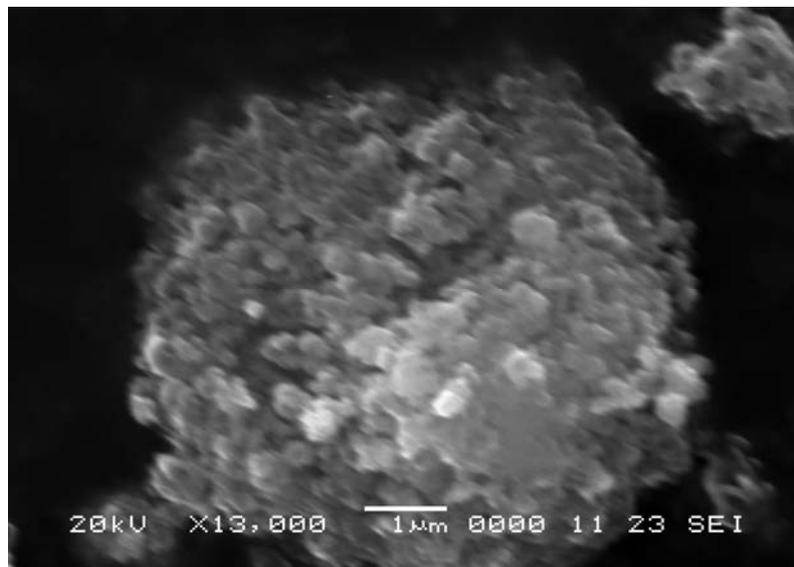

Figure 2: SEM shows cluster of particle of the produced powder at magnification of 13,000
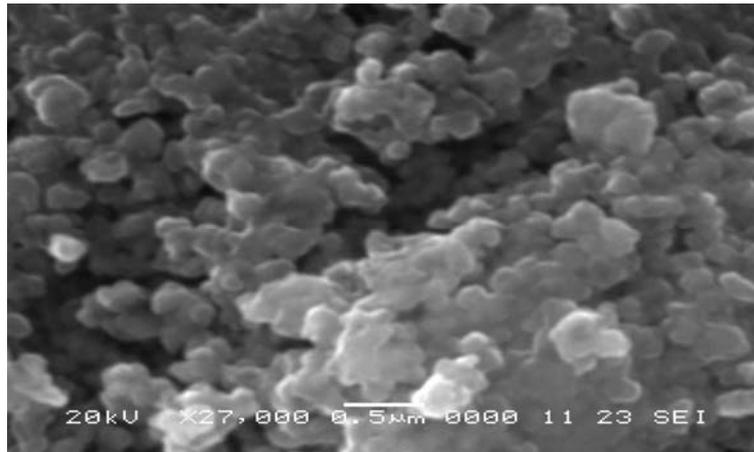
Figure 3: SEM shows the particle size of the produced powder at magnification of 27,000
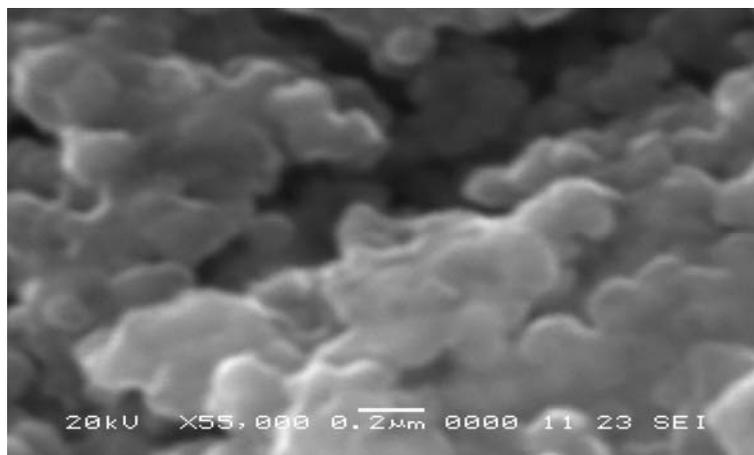

Figure 4: SEM shows the particle size of the produced powder at magnification of 55,000

Effect of Temperature

The experimental conditions used for the effect of temperature investigation are detailed in Table (1), where three values of the temperature was selected at 10 $^{\circ}$C, Room temperature and 80 $^{\circ}$C. The other parameters were kept constant. The results of analysis of the effect of this parameter variation showed that a nano-size particle of 35.89nm is produced at 10 °C, whereas a particle size of 22.5 nm is produced at room temperature and a particle size of 18.08 nm is produced at 80 $^{\circ}$C. The change of temperature has a noticeable effect on the size of the produced particles. This is due to the effect of temperature on the crystallization kinetics, i.e., the rate of crystallization as well as the rate of growth of crystals depends upon the crystallization temperature.

Table 1: Effect of temperature on the particle size

No	Stirring time (min)	Stirring Speed (rpm)	Addition method	Temp.($^{\circ}$C)	Size (nm)
1	10	750	One portion	R.T	22.54
2	10	750	One portion	80	18.08
3	10	750	One portion	10	35.89

Effect of Stirring Speed

The second parameter of the experimental set up used in the preparation of Magnesium oxide nano-size particle is the stirring speed. Three different levels; 250 rpm, 750 rpm and 1250 rpm, were considered. The level range values selected for this parameter is found to have no effect on the particle size of the nano-powder which is estimated to be 22.5 nm as shown in Table (2).

Table 2: Effect of stirring speed on the particle size

No	Stirring time (min)	Stirring Speed (rpm)	Addition method	Temp. (^{o}C)	Size (nm)
1	10	250	One portion	R.T	22.54
2	10	750	One portion	R.T	22.54
3	10	1250	One portion	R.T	22.54

Effect of Dilution of Magnesium Nitrate Solution

The effect of dilution of magnesium nitrate was investigated by adding 300 ml and 600 ml of distilled water to the 300ml of 0.01M solution of magnesium nitrate. The nano-size particle produced at the three levels of magnesium nitrate concentration is 22.5nm, which means that the dilution has no effect on the particle as presented in Table (3).

Table 3: Effect of dilution on the particle size

No	Stirring time (min)	Dilution (Distill. Water added) (ml)	Stirring Speed (rpm)	Addition method	Temp. (^{o}C)	Size (nm)
1	10	300	750	One portion	R.T	22.54
2	10	600	750	One portion	R.T	22.32
3	10	900	750	One portion	R.T	22.32

Effect of addition Method

In this experimental condition, the effect of addition of the solutions to each other is the aim of this experimental runs. Two ways of addition were tried keeping the other experimental parameters unchanged as presented in Table (4). The method of addition of the solutions has no significant effect on the particle size yielded under these experimental conditions. Having the solutions added to each other in one portion or four equal portions has no effect on the size of produced nano-particles which is 22.5 nm.

Table 4: Effect of addition method on the particle size

No	Stirring time (min)	Stirring. Speed (rpm)	Addition method	Temp. (^{o}C)	Size (nm)
1	10	750	One portion	R.T	22.54
2	10	750	4 equal portions	R.T	22.43

CONCLUSION

A comprehensive study on the nano-sized MgO material has been conducted to understand the mean features characterized this class of structure due its importance in

the modern technology. A nano-particle size of MgO is produced by wet chemical technique where parameters such as temperature, stirring speed, addition method and concentration of solutions were controlled using three levels of each parameter.

The particle size obtained by using XRD is in the range (18 – 36 nm) where the temperature parameter was the most pronounced effect on the used technique for producing the MgO particle. Three different values for the particle size produced by this method as a function of temperature as the effective parameter are 36 nm at 10 $^{\circ}$C, 22.54 nm at room temperature and 18nm at 80 $^{\circ}$C

The other three parameters have no detectable effect on the particle size produced by this technique, and this result may be due to sensitivity of the devices used in the characterization process of the produced particle; the other possible reason is the selection of the level range of these parameters was not right and it may need adjustment. In other words, the factors that affecting the characteristics of conventional precipitate have no noticeable influence on the characteristics of nano-particles precipitate.

REFERENCES

[1]   Siegel, R. W., Nanostructure Mater. 1993, 3, p.1-8
[2]   Kuhn, E., Ultrafine Particles, (ed. W.E. Kuhn), 1963, 41-103, New York, Willey
[3]   Charvant, F. R., and W. D. Kingery, J. Am. Ceram. Soc. 1957, 40, p. 306.
[4]   Gleiter, H., Prog. Mat. Sci., 33, 1989, p. 223.
[5]   Zhu, R. X., Birringer, U. and H. Glether, Phys. Rev. B, 1987, 35, p. 9085.
[6]   Ganapathi, S. K., Owen, D. M. and A.H. Chokshi, Scripta Metall. et, Mater.1991, 25, p. 2699.
[7]   Keblinski, P., Phillpot, S. R. and D. wolf, phys. Rev. Lett., 1996, 77, p. 2965.
[8]   Keblinski, P. Phillpot, S. R., wolf, D. and H. Gleter, Nanost. Mat., 1997, 9, p. 651.
[9]   Glether, H., Second Riso Int. Symp. Metallurgy and Mater. Sci., ed. N. Hansen, A. Horsewell and H. Lilholt, Denmark, 1981, 15
[10] S.P. New Berry, EMSA, The first fifty years, Boston, MA, Electron Microscopy Society of American, 1992 ,67.
[11] R. Schulz (ed.), Mater. Sci. Forum, 1996, vol. 225-227.
[12] Schonert, K., Advances in material processing, (ed. P. somasundaran) Littlrton, CO, Society of mining Eng., 1986, p. 19.
[13] Mayo, M. J., International Materials Review, 1996, 41, 3, p. 85.
[14] Pampuch, R. and K. Haberko, Ceramic powders, (ed. P. Vincenzini), Amsterdam, Elsevier Scientific Publ. 1983, p. 635.
[15] Fecht, H. J., Hellstern, E., Fu, Z. and W.L. Johnson, Metall. Trans.,1990, 21A, p. 2333.
[16] Whittemore, O. J., Posder Technol., 1981, 29, p.167.
[17] Roosen, A. and H. Hausner, Science and Technology of Zirconia, 2, 1985, (Adv. In Ceram., vol. 12), p. 714.
[18] Innes, W. B., Expedite methods in catalytic research; Anderson, R.B. Ed. Academe pres New York, 1986.
[19] Suchad, U. K., Nanoscale Metal oxide Particles clusters and chemical Ragouts chem... Mater, 1991, 3.