PREPARATION AND CHARACTERIZATION OF PURE IRON NANOPARTICLES USING HIGH ENERGY BALL MILLING

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الملخص

تحضير مساحيق ذات جسيمات متناهية الصغر (نانومتريه) (Nanoparticles) باستخدام آلة طحن عالية الطاقة استحوذ على اهتمام كبير من البحاث في السنوات الاخيرة لبساطته وكلفته المنخفضه نسبيا. في هذا البحث استعملت عملية الطحن لإنتاج مسحوق الحديد ذو جسيمات متناهية في الصغر وتم دراسة تأثير زمن الطحن وكذلك الوسط المبلل الايثانول (Ethanol) على عملية الطحن. النسبة الوزنيه بين كرات الصلب والمسحوق ثبتت عند نسبة 1:4 وبعد انتهاء عملية الطحن جمعت الحبيبات باستخدام مجال مغناطيسي وجففت عند درجة حرارة 80 ^{o}م. تم بعد ذلك فحص هذه الحبيبات باستخدام مجهر المسح الالكتروني (SEM) وحيود الاشعة السينية (X-ray diffraction) وأثبتت هذه الفحوصات أنه تم بنجاح الحصول على جزيئات من الحديد متناهية الصغر (Nanoparticles) يتراوح حجمها ما بين 29 – 38 نانومتر.

ABSTRACT

The preparation of nanoparticles powder by high-energy ball mill has drawn considerable attention in recent years for its simplicity and relatively low cost.

In this research work milling process was utilized to produce nanoparticles iron powder. The effects of milling time as well as the wetting agent (ethanol) on the milling process, were investigated. The ball to powder weight ratio was fixed at 4:1 and after milling process the produced particles were collected using a magnetic field and then furnace dried at a temperature of 80 ^{o}C. The collected particles were characterized using scanning electron microscopy (SEM) and x-ray diffraction.

High-resolution scanning electron microscopy (HRSEM) images and x-ray diffraction (XRD) confirmed that ball milling has successfully produced iron nanoparticles with approximately 29- 38 nm in size.

INTRODUCTION

Many of the principles used in the fields of physics, chemistry and biology are based on the use of large, or macromaterials. Within the last few decades, scientists have opened up a completely new world of materials called nanoparticles. A Nano object is a physical object differing appreciably in properties from the corresponding bulk material and having at least 1 nm dimension (not more than 100 nm).

Nanomaterials are those materials with nanometre sizes in one, two or three dimensions. A nanoparticle is a quasi-zero-dimensional (0D) nanoobject in which all characteristic linear dimensions are of the same order of magnitude (not more than 100 nm). Nanorods and nanowires are quasi-one-dimensional (1D) nanoobjects. In these systems, one dimension exceeds by an order of magnitude the other two dimensions, which are in the nano range. The group of two-dimensional objects (2D) includes planar structures nanodisks, thin-film magnetic structures, magnetic nanoparticle layers, in

which two dimensions are of an order of magnitude greater than the third one, which is in the nanometer range. When dealing with nanoparticles magnetic properties and other physical ones are, to a large extent, size dependent.

In recent year's nanoparticles and nanoparticles technologies have attracted increasing attention for their great and wide potential applications [1-7]. Nanomaterials have unique physical, chemical and mechanical properties that are neither those of bulk materials nor those of molecular compounds.

KEYWORDS: pure iron nanoparticles; iron powder; high-energy ball milling; mechanical milling; wet milling

EXPERIMENTAL WORK

Starting Materials

As received iron, powder of 99 % purity, manufactured by the Alfa-Aesar Company (Germany), was used as a starting material in this work. The used powder has an average particle size of approximately five μm in diameter and a density of 7.87 g/cm^3. Ethanol was used as the wetting medium.

Mechanical milling equipment

Milling of iron powder was performed using a laboratory high-energy centrifugal ball mill available in the department, [Model S100, Retsch GmbH], Figure (1).

Figure 1: A picture of the centrifugal mill used in the present work

The used centrifugal ball mill is suitable for ultrafine batch, wet and dry, grinding. Extremely high centrifugal forces brought about by the special design of the drive mechanism achieve a high degree of fineness and excellent mixing and homogenization of the batch in extremely short time.

Samples preparation

Wet milling was carried out in a 250 ml special steel jar using 10 mm diameter stainless steel balls and with each milling run having a different time and quantity of the liquid medium. The weight ratio of the steel balls to iron powder was chosen to be 4:1. The jar was loaded with a fixed amount of 30 grams of the iron powder and 120 grams of stainless steel balls for all runs. The milling time varied from 2 to 4 hours with increment of 10 minutes for each set of mixture which was suitable to obtain nano range. The powder was milled at room temperature. The rotation of ball mill was reversed every 35 seconds.

This reversing operation is useful when long term grinding operations (>1 hour) and wet grinding have to be performed. The speed of the ball mill was set at 550 rpm. After milling process the produced particles were collected using a magnetic field and then furnace dried at a temperature of 80 ^{o}C for half an hour to remove the excess ethanol. During drying process powder cohesion has occurred, for this reason the powder was milled again for 10 mins to separate the particles from each other. Six different samples were prepared as shown in Table (1). The effects of milling time as well as the quantity of wetting agent (WA) (Ethanol), on the milled powder particle size, were investigated using x-ray diffraction technique and SEM microscope.

Table 1: Ethanol quantity and milling time for the prepared samples.

Sample number	1	2	3	4	5	6
Milling time (hours)	2	2	3	3	4	4
Ethanol quantity (ml)	10	20	10	20	10	20

X-ray diffraction

The x-ray diffraction was used to estimate the particle size of milled powder particles. The x-ray diffraction patterns were taken using a computerized x-ray diffractometre (Model: PW 1800 of M/s Philips NV, Holland) at the industrial research centre, Tripoli-Libya. All x-ray diffraction patterns were taken by Cu-K_{α} radiation (wavelength, λ = 1.5406Å). It is well established that changes in the shape and width of x-ray peaks are associated with changes in the particle size, lattice strain and defects in the material [8]. Small particle size, heavy strain and large number of defects result in the broadening of diffraction peaks and the change in peak shape as well. Diffraction peaks of materials with large particle sizes tend to have a Gaussian line shape while the diffraction peaks of materials with small particle sizes tend to have a Cauchy line shape.

In the present work, milled powders had sub-micron particle size. Therefore, their peak shapes were considered to be of a Cauchy shape. The particles size of milled powders were estimated from the broadening of x-ray diffraction peaks using the well-known Scherrer's formula [8,9]. According to this formula, the average particle size (t) can be estimated from the full peak width (B) at half maximum intensity, as follows;

$$t = \frac{0.9\,\lambda}{B\cos\theta_B}$$

Where, 0.9 is a constant, λ is the wavelength of incident x-ray and θ_B is the incident angle in degrees.

Scanning electron microscope

The scanning electron microscope (SEM, at the Libyan Petroleum Institute), was also used to image the morphology of the samples. Representative images are shown in Figures (3) and (4).

RESULTS AND DISCUSSION

X-ray diffraction analysis

The x-ray diffraction was used to estimate the particle size of milled powder particles. The average particle size was estimated according to the Scherrer's formula given above. A representative diffraction patterns is given in Figure (2).

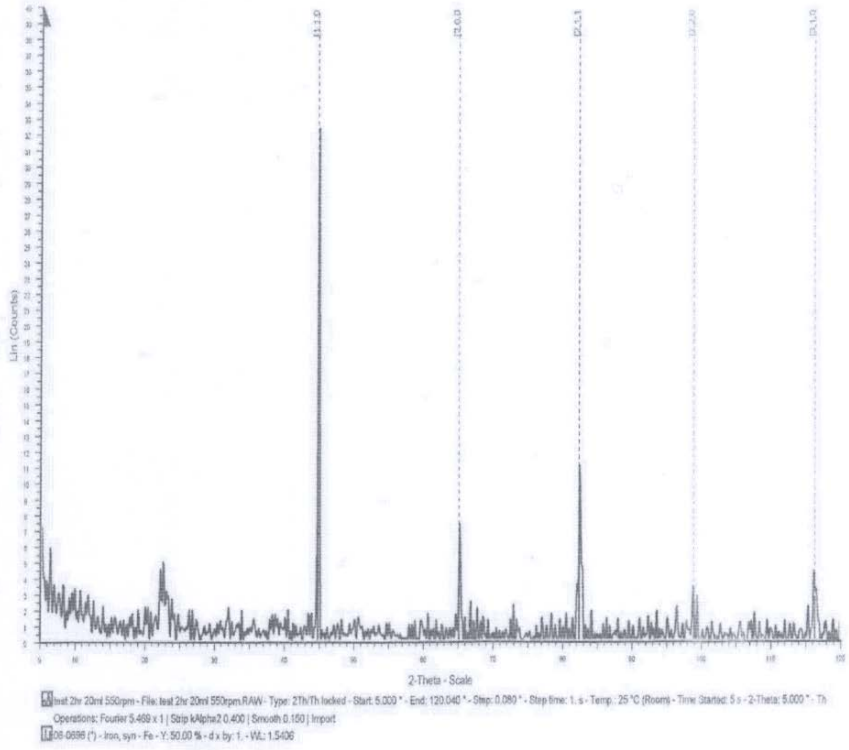

Figure 2: X-ray diffraction pattern for sample number 2 (2 hr and 20 ml)

The x-ray diffraction patterns analysis data are given in Table (2) and presented graphically in Figure (5).

Table 2: Results of x-ray diffraction patterns analysis

Sample No.	1	2	3	4	5	6
θ (degrees)	22.30	22.30	22.30	22.30	22.30	22.30
B (radians)	0.0048869	0.0041887	0.0045378	0.0039269	0.0050614	0.0052359
t (nm)	30.67	35.78	33.03	38.16	29.61	28.62

Scanning electron microscope micrographes

Figures (3) and (4) show the SEM images of pure iron nanoparticles as prepared by high energy ball mill technique. The particles of the pure iron have a smooth surface and sizes of about 29–38 nm, while the morphology was nearly spherical.

Iron powder was converted to nanometre sized particles after they were milled at three different times by using a high energy ball milling technique. During high-energy ball milling (HEBM) the powder particles are repeatedly flattened, cold-welded, fractured and re-welded. However, for a certain period of milling time of elemental ductile components, steady-state equilibrium is attained when a balance is achieved between fracturing and cold welding of particles, which leads to a rather stable average particle size. The nanometric particle size obtained after HEBM, was as a result of the reduction in the cold welding processes which also promotes fracturing and the particle size decreases with increasing milling time. This was achieved by the addition of ethanol as a processing control agent.

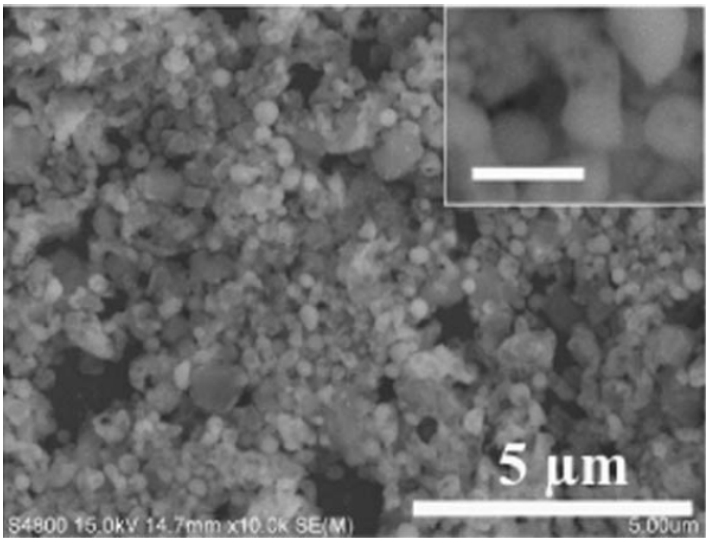

Figure 3: Shows the SEM image of pure iron nanoparticles, sample 2 (2 hrs, 20 ml)

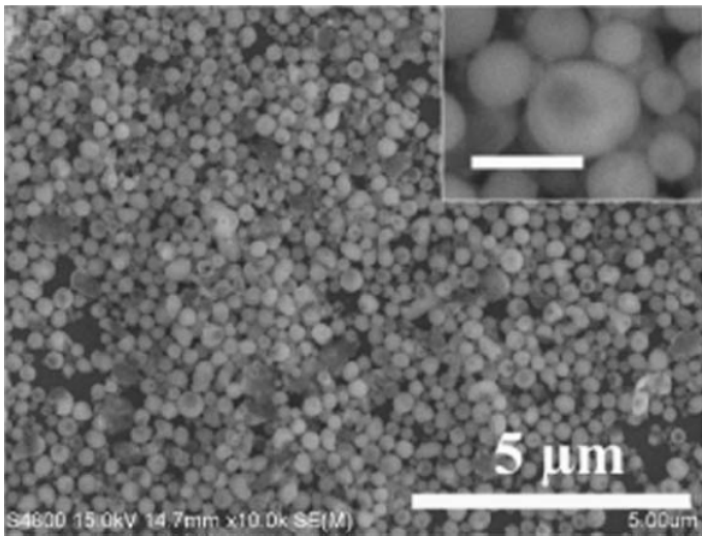

Figure 4: Shows the SEM image of pure iron nanoparticles, sample 6 (4 hrs., 20 ml)

Effect of milling time and wetting agent (WA)

The wet milling technique is well used to fine-tune the particle size of the materials in to nanoscales. Wetting agent (WA) was used to reduce the aggregation of particles**.** During further milling, the WA has a lubricating effect that minimizes the cold welding effect. Without the WA, the powder being milled welds on the milling jar walls resulting in only a fraction of the charge load being recovered. The welding also increases downtime between milling runs.

The introduction of 10 ml WA did not change the particle size significantly; increasing the WA amount to 20 ml decreased the particle size from 37.73 to 28.30 nm with different times of milling. The evolution of the particle size distribution for this WA content suggests that the process of powder particle fracture had dominated cold welding during milling. The influence of the various WA amounts on the particle sizes are shown in Table (2) and Figure (5).

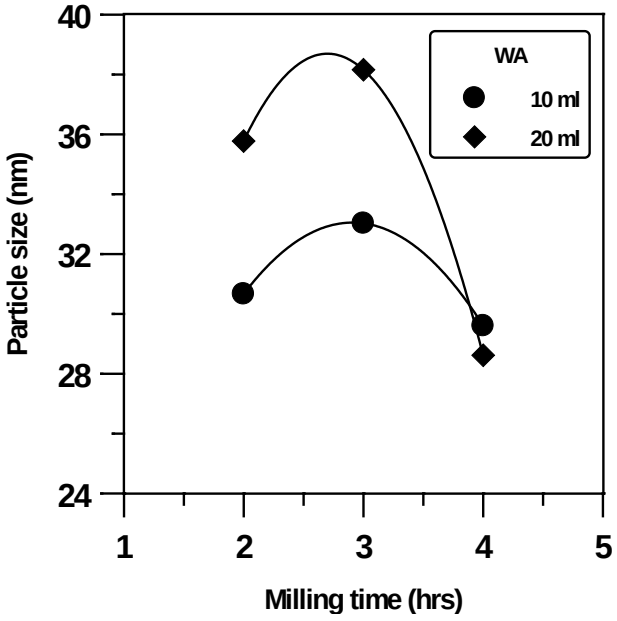

Figure 5: The effect of milling time and WA on the particle size of milled powder

CONCLUSIONS

Based on the results obtained in this paper the following conclusions can be drawn:

- High energy centrifugal ball milling can lead to the preparation of iron powder particles in the nano size range.
- The nano-scale iron particles were obtained as a result of the reduction in the cold welding processes, which promotes fracturing.
- In Fe-HEBM, the particle size of the powder decreases with increasing milling time; however, the particle size does not decrease linearly with milling time.
- The current work suggests that this characteristic milling duration will have to be determined each time a new WA amount is chosen for milling.

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