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The Effect of Raw Materials Molar Ratio in Mechanochemical Synthesis of Amorphous Fe-B Alloy Nanoparticles

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In this study, amorphous iron-boron alloy nanoparticles successfully synthesized by mechanochemical method. The raw materials were ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) as a source of iron and sodium borohydride ($NaBH_4$) as a reducing agent. Powders grinding was performed with different $NaBH_4/FeSO_4.7H_2O$ molar ratio. The results revealed that high active and completely amorphous particles could be synthesized with the molar ratio of 4:1 for $NaBH_4$:$FeSO_4$ in 10 minutes of grinding time. Various characterizations, such as the chemical analysis, atomic absorption spectroscopy (AAS), fourier transform infrared spectroscopy (FT-IR), x-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) have been performed. The XRD results confirmed the formation of the amorphous phase. Other results also indicate the formation of amorphous alloy nanoparticles with an average particle size below 50 nm and the composition was Fe-10 Wt % B.

Keywords: Amorphous, Nanoparticles, Fe-B alloys, Mechanochemical, $NaBH_4$, Grinding.

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1. INTRODUCTION

Amorphous alloys as important materials were used due to mechanical properties, corrosion resistance, magnetic and catalytic behavior. Among these amorphous alloys materials, the iron-boron alloy is known due to soft magnetic properties [1-2]. This alloy usually produced by the melt-spinning method, which produce amorphous thin ribbon at high temperatures and rapid cooling [3-4].

Both mechanical alloying and chemical reduction methods have been studied to produce amorphous Fe-B alloy nanoparticles [5-6]. The mechanical alloying method was reported to produce amorphous phase after many hours high energy ball grinding of pure iron and boron powders as raw materials [6]. The formation of amorphous alloy nanoparticles of Fe-B was studied by reduction of Fe^{2+} ions with BH_4^- ions in the iron salt and potassium borohydride aqueous solution. A series of studies on reduction technique have been revealed that reaction conditions, such as concentration , ratio of the reactants, pH value of the solution, mixing procedures and reaction temperatures, etc., have signif-icant effects on the composition and structure of amorp-hous nanoparticles [7-10].

Although, the above methods were used to produce amorphous alloys, the mechanochemical method is a simple solid-state reaction technique for the synthesis of nanoparticles [11]. In this method, the desired phase and particle size will be achieved by changing parameters such as type of mill, grinding time, ball to powder ratio and molar ratio of raw materials. This process is carried out in one step at low temperature [12-13]. Zhou et al. [11] were prepared Fe-based amorp-hous alloy nanoparticles by solid state reaction method at room temperature using powders of iron chloride and chromium chloride with potassium borohydride as raw material. In this study, the amorphous iron-boron alloy nanoparticles have been synthesized with difference molar ratios of iron sulfate hydrated and sodium boro-hydride which are new raw materials for this approach.

2. EXPERIMENTAL PROCEDURES

All the chemical materials used in the experiments were analytical reagent grades. The used raw materials were $FeSO_4 \cdot 7H_2O$ (99.98 %, Merck), and $NaBH_4$ (99 %, Merck). The mol ratio of $FeSO_4$: $NaBH_4$ are listed in Table 1. The $FeSO_4$.and $NaBH_4$ mixtures powders were placed in an agate mortar and were grinded carefully at room temperature for 10 min. Since the reaction is associated with gas release, the milling is dangerous in a closed vial. After grinding, the mixture color changed from white to black. This indicated that the reaction has been occurred.

Table 1 – Raw materials were used for the preparation of Fe-B amorphous alloy.

Sample	$NaBH_4$ (mg)	$FeSO_4$ (mg)	Molar ratio $NaBH_4$: $FeSO_4$
S_1	0.67	2.48	2:1
S_2	1.34	2.48	4:1
S_3	2.02	2.48	6:1

The black product was moved to a glass beaker as soon as possible. At first, the product was washed carefully with a large amount of deionized water for several times to remove residual ions from the reaction mixture, followed by washing with acetone to remove the water, and then collected by a centrifugation sytem. The acetone wet slurry on crucible was transferred to a box with slow flow of high purity argon gas (less than 100 ppm of oxygen) and maintained for 4 h to dry the sample and passivate the surface of the particles. Lack of passivation will lead to pyrophoric samples. The final product is fine black particles.

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The composition of the product was determined by the atomic absorption spectroscopy (AAS; Varian-Spectrum AA220). The vibrations of atoms in the region from 400 to 4000 cm^{-1} of the resultant were measured by a Fourier transformation infrared spectroscopy (FTIR; Perkin Elmer-Spectrum Frontier) and the potassium bromide disk technique. The phase study in samples was characterized by X-ray powder diffraction (XRD; Xpert-Philips) analysis with Cu Kα radiation. The mophology and particle sizes of the product were also studied by a field emission scanning electron microsc-opy (FE-SEM; Hitachi) system equipped with an energy dispersive X-ray (EDX) spectrometer for the elemental analysis of the amorphous alloy nanoparticles.

3. RESULTS AND DISCUSSION

The observations showed that black powder was formed from white raw materials after grinding. This indicates that the reaction has occurred. Based on the reaction of ferrous sulfate heptahydrate and sodium borohy-dride, the following equations has been occurred and the colorless released gas during the grinding was H_2.

$$FeSO_4 + NaBH_4 \rightarrow 2Fe + HBO_2 + HNaSO_4 + 2H_2 \quad (1)$$

$$NaBH_4 + H_2O \rightarrow B + NaOH + 2.5H_2 \quad (2)$$

Black particles sticking to the magnet, during washing the powders with electromagnetic stirrer, revealed that the particles are magnetic. Also, the formation of yellow fine particles on beaker wall was observed during washing process which indicate the oxidation of the particles.

The results of atomic absorption spectrometry (AAS) are shown in Table (2). Analysis shows that the particles have an average of 90 % iron and 4 % boron. The total amount of iron and boron is about 94 %. As mentioned above, amorphous iron-boron alloy nanopaticles could be oxidized easily with oxygen in the air. Therefore, another most possible element except for iron and boron in the poroduct, could be oxygen. In this case, the content of the oxygen in the nanoparticles might be about 6 % which might present on the surface of iron-boron particles. Also the results show that with increasing the molar ratio of $NaBH_4/FeSO_4.7H_2O$, the amount of boron in the alloy composition is increased.

Table2– Results of atomic absorption spectroscopy.

Sample	B (wt %)	Fe (wt %)
S_1	3.3	90
S_2	4.1	89.9
S_3	6	88

Fig. 1 shows the X-ray diffraction pattern of S_1, S_2 and S_3. As can be seen, there is no diffraction peak in the S_2 and S_3 samples, so that the S_2 and S_3 products are amorphous compounds. Only a broad peak at 46° angle can be seen. This is very close to the characteristic diffraction peak of α-iron crystal at 45° degrees for (110) plane. It indicates that the product is mainly composed of large amounts of iron. The small peak at 35° angle in the S_3 diffraction pattern is very close to the characteristic diffraction peak (200) from Fe_2B. This indicates that the product is mainly composed of large amount of Fe and small amount of Fe_2B. It can be noted that the presence of boron in the iron lattice has helped to form amorphous Fe-B alloys. The broad peak shifts in S_3 from 45° to 46° is probably due to the presence of boron in iron lattice. In other words, it is well known that any increasing of boron content in compound can increase the possibility of amorphous phase formation. In compliance with the AAS and XRD results, increasing in molar ratio of $NaBH_4/FeSO_4.7H_2O$ from 2 to 4, increase the amount of boron in alloy composition and amorphous phase formation but then decrease it. Thus, it is not necessary to use a molar ratio much higher than 4 as adopted in some literature [11]. The optimal and suitable value for the preparation of amorphous Fe-B alloy nanoparticles can be considered to select 4 for molar ratio of $NaBH_4/FeSO_4.7H_2O$.

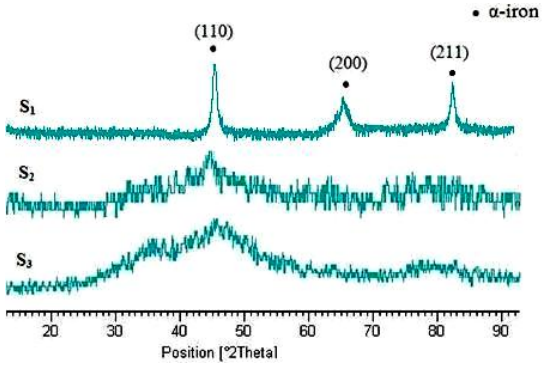


Fig. 1 – X-ray diffraction for crystalline iron S_1, S_2 and S_3 amorphous Fe-B alloy nanoparticles

The FESEM images in Fig. 2 show the morphology and particle size of amorphous Fe-B alloy nanoparticles. As the images show, the particles have spherical shape with the average size of less than 100 nm. High surface energy and high activity of thermodynamically unstable amorphous nanoparticles lead to agglomeration of iron-boron nanoparticles. In the higher resolution images of the nanoparticles, it could be seen that the particles size is below 50 nm in the great separation of agglomerated particles.

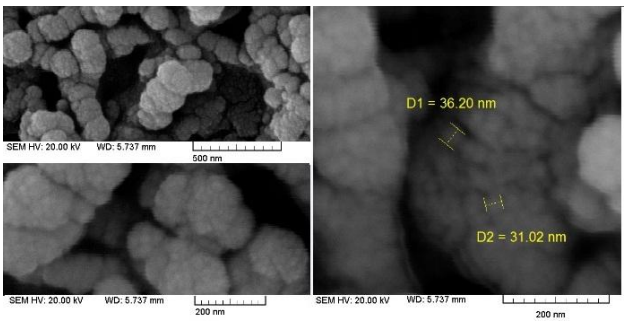
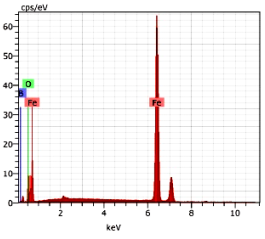


Fig. 2 – The FESEM micrographs of amorphous Fe-B alloy nanoparticles

Fig. 3 shows the Energy Dispersive X-ray analysis of the images for S_2 sample. It has a good agreement with the composition analysis results of the product by atomic absorption spectroscopy.



El	AN	Series	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]
Fe	26	K-series	84.83	55.52	2.4
B	5	K-series	8.96	30.30	2.9
O	8	K-series	6.21	14.18	1.0
		Total:	100.00	100.00	

Fig. 3 – The EDX analysis for S_2 sample

Formation of amorphous iron-boron alloy nanoparticles by mechanochemical method through the grinding of ferrous sulfate heptahydrate and sodium borohydri-de is due to thermodynamically instability of $NaBH_4$ and it has a great affinity for reduction. Therefore, the $NaBH_4$ can react with the $FeSO_4.7H_2O$ as easily as possible.

The infrared spectrum in Fig. 4 demonstrates four shoulders at around 668.99, 1456.44 and 2359.23, 3851.80 cm^{-1}. Generally, the transmittance peaks from the vibration of the metal–metal bond are in the region (< 400 cm^{-1}) of the far-infrared spectra [11]. Therefore, the peak at 668.99 cm^{-1} in the infrared spectra may be assigned to the stretching vibration of the Fe–B bond in the product. It can be concluded that iron and boron atoms are willing to form the alloy. Higher peak is related to the hydrocarbon and water vapor in the air that has been recorded.

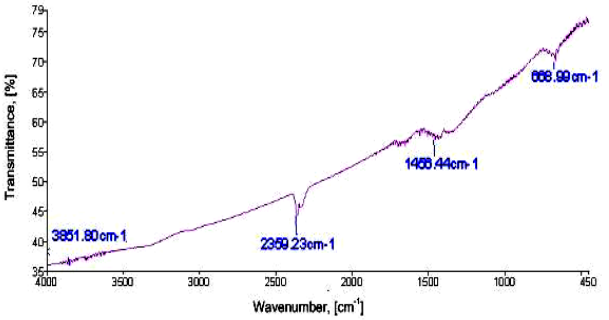


Fig. 4 – The FTIR spectrum of amorphous Fe-B (C, O, H) alloy nanoparticles

It should be noted that the mechanochemical reactions, during grinding at room temperature, is mainly a surface reaction. The reaction occurs only on the interface layers between the molecules or ions of the particles of $FeSO_4.7H_2O$ and $NaBH_4$ powders. After the reaction on the surface, the product will be peeled off right away from the surface of the particles of the hydrated iron sulfate powders due to the grinding of the reacting powders. Hence, the primary product consists of some atomic clusters. Unlike the high temperature solid state reaction, the structural arrangement or crystallization in the atomic clusters of the product are rather slow at room temperature. Perhaps, this is just why the amorphous iron boron alloy nanoparticles can thus be obtained very easily by mechanochemical method at room temperature.

Although the above product contains some iron oxides due to the oxidation of the iron boron alloy particles, the oxidation of the fresh iron boron alloy nanoparticles can be avoided in the preparation process by using the inert gas atmosphere.

4. CONCLUSIONS

Mechanochemical method is a convenient and practical way for synthesis of amorphous Fe-B alloy nanoparticles. Amorphous Fe-B alloy nanoparticles can very easily be prepared through the reaction of ferrous sulfate heptahydrate and sodium borohydride powders. By increasing the molar ratio of $NaBH_4/FeSO_4.7H_2O$, the amount of boron in the alloy composition was increased and the amorphous phase formation was more favorable. The optimal and suitable molar ratio of $NaBH_4/FeSO_4.7H_2O$ for the preparation of amorphous Fe-B alloy nanoparticles is 4. The results of various characterizations indicate that the product is mainly amorphous Fe-B alloy nanoparticles with a diameter below 50 nm and contains fine iron oxides nanoparticles due to the surface oxidation.

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