

Investigation of nano iron carbide production by ball milling

E. EVİN*

Department of Metallurgical and Materials Engineering, Faculty of Eng., Firat University, Elazığ 23119, Turkey

In this study, two routes were used in order to produce iron carbide. Graphite powders were amorphized and reduced to nano-size by ball milling process for C source. And also, nano-porous hematite powders were produced by thermo-mechanical method. In first route all powders, graphite and hematite were milled individually. In second route, both graphite and hematite were milled together up to 20 hours in a planetary ball mill. The nano-sized powders obtained from route one and two were compacted in order to make pellets. Then, these compacts were sintered in different temperatures between 800, 900 and 1000 °C. The samples were investigated by X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM) and Wavelength Dispersive X-Ray (WDX) in order to determine structural and morphological changes.

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1. Introduction

The nano-crystalline iron carbide (Fe_3C , cementite) can serve as an iron based composite for the preparation of materials used for construction of machines or equipment [1]. Such materials have new, better mechanic properties compared with the traditional ones. The nanocrystalline carbides of iron are also interesting because of their particular magnetic characteristics.

Usually, metal carbides are prepared by conventional ceramic route, which requires a very high temperature as well as good vacuum condition or ultra-pure inert gas atmosphere. However, nanocrystalline metal carbides with homogeneous composition can be prepared at room temperature by mechanical alloying (MA) the stoichiometric mixture of elemental powders under inert atmosphere.

Mechanical alloying process is a very useful solid-state technique for production of high melting point compounds like metal carbides and nitrides, which additionally have nanocrystalline structure with improved properties [2–5]. If the Fe–C system is composed of a very fine microstructure, which can be synthesized by MA, it is possible to produce an advanced material with high hardness, wear resistance, toughness and good magnetic properties.

In this study, iron carbide were produced by two different routes. In first route, graphite and commercial hematite powders were milled separately up to 20 hours by a high energy ball mill. The graphite powders were amorphized and reduced to nano-size by ball milling process. And also nano porous Fe_2O_3 powders were synthesized by ball milling and annealing processes. Then, amorphous graphite and Fe_2O_3 powders were mixed by powder metallurgy methods. In second route, graphite and hematite powders were milled together. Powders which

prepared via both first and second route were pelleted and were sintered at different temperatures between 800 and 1000 °C. The obtained samples were investigated by XRD analysis in order to determine structural change. Microstructure analyses of samples were investigated by using Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscope (TEM).

2. Experimental details

2.1. First route

At this route, nano porous Fe_2O_3 powders were synthesized by ball milling and subsequent annealing processes. Firstly, pure Fe powders (Merck % 99, 9 purity and $D_{50}=30 \mu\text{m}$ particle size) were milled under air atmosphere in a planetary ball mill (Retsch PM 200 model) for decreasing of particles size. Milled powders were annealed then re-milled and this process was repeated up to 20 hours for each treatment step. The milling speed was 200 RPM, Ball to Powder Ratio (BPR) 20:1, ball diameter was 8 mm and hardened steel vials were used. Annealing process was performed at 550 °C in air atmosphere. Total processing time both milling and annealing were performed for 10 and 20 hours. Synthesized powders were characterized by X-ray (XRD) diffraction (Bruker D8 Advance, with CuK_α radiation) and Field Emission Scanning Electron Microscopy (FESEM, Jeol; Jsm-7001F) and TEM (Joel 2100F). By this way, nano porous Fe_2O_3 powders were produced.

As an Carbon source, hexagonal graphite (Merck 99.5%) were milled for 20 hours. A high energy planetary ball mill, Retsch PM 200, was used with a rotational speed of the vial at 500 rpm and hardened steel vials were used. The ball milling was carried out by 8 mm balls (100Cr4)

and BPR was 20:1. The structural characterizations of the milled samples were investigated by the same XRD instrument model given before with CuK α radiation.

For nano Fe₃C production, amorphous-C obtained from milled graphite powders and nano porous Fe₂O₃ powders were mixed as stoichiometric rates and compacted. And then, they were sintered at different temperatures as is 800, 900 and 1000 °C. The sintered samples were investigated by XRD analysis in order to determine structural change. Microstructure analyses of samples were investigated by using FESEM which the same brand given in the first route.

2.1. Second route

In this route, the same graphite (Merck 99.5%) and commercial iron oxide (Fe₂O₃, Alfa Aesar, 12375) powders were used as the starting material. Graphite and hematite powders were mixed as stoichiometric rate and then were milled together for 20 hours in Ar atmosphere. The milling experiments were performed in Retsch PM 200 with a rotational speed of the vial at 500 rpm. Milled powders were compacted in order to make pellet. And then, samples were sintered at different temperatures as is 800, 900 and 1000 °C. The obtained samples were investigated by FESEM and XRD in order to determine structural/morphological changes..

3. Results and discussion

Using of hematite (Fe₂O₃) and carbon is first idea from reduction of hematite for the producing of iron carbide. The reactions in the hematite-carbon composite pellets are classified as direct reductions and indirect reductions. The indirect reductions are a reduction which made by CO gases. But, direct reduction was carried out by solid carbon atoms. With the assumption that the total amount of reduction of iron oxides by CO is equal to the amount of the carbon solution loss reaction, the overall reduction can be expressed as Fe₂O₃ + 3C = Fe + 3CO [6-7]. In this study, the stoichiometric rates were considered according to the reduction of hematite formula.

3.1. First Route

Fig. 1.a illustrates the XRD pattern of unmilled iron and synthesized nano porous Fe₂O₃. The different peaks in the XRD pattern of the synthesized Fe₂O₃ samples were appeared at 2 θ values, 24,142°, 33,152°, 35,611°, 40,857°, 49,472°, 54,095°, 57,583°, 62,461°, 63,98° and 72,253° corresponding to (012), (104), (110), (113), (024), (116), (018), (214), (300) and (119) reflections, respectively. 10 hours milled and 10 hours annealed samples were not fully transformed to Fe₂O₃ but after 20 hours milling and 20 hours annealing, thermo-mechanical treatment, nano porous Fe₂O₃ were obtained successfully. Fig. 1b shows the TEM image of nano porous Fe₂O₃. The porous structure is clearly can be seen from the figure.

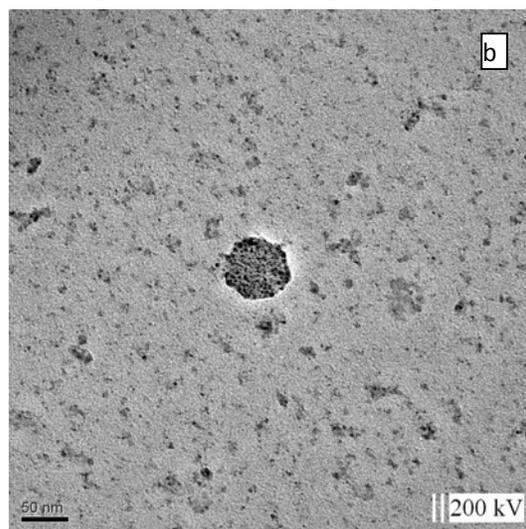
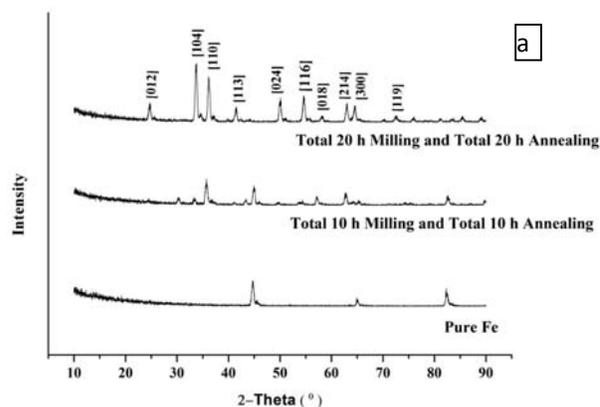


Fig. 1a, b. a) XRD pattern; b) TEM image of synthesized nano porous Fe₂O₃

X-ray diffraction measurements were used to determine the nature of the milled powders and the structural characteristics of pure iron and nano porous Fe₂O₃. The crystallite size of the investigated materials can be calculated from the X-ray data by means of full width at half maximum (FWHM) method known as Scherrer's equation [8]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where β is the full-width at half maximum of the XRD peak appearing at the diffraction angle θ . From Scherrer's equation, the crystallite sizes of nano porous Fe₂O₃ samples were calculated as 37,9 nm.

Fig. 2 illustrates the XRD pattern of the graphite powders which were unmilled and were subjected to 20 hours milling process. Unmilled graphite powder has a hexagonal structure and consists of a series of stacked parallel layer planes. From the figure, the XRD pattern of the hexagonal graphite consists of the characteristic (002) peak and other peaks (004, 110). After 20 hours milling process, these peaks have completely become lost in other

words the structure has completely amorphised. By this way, it can be said that amorphous-C was obtained.

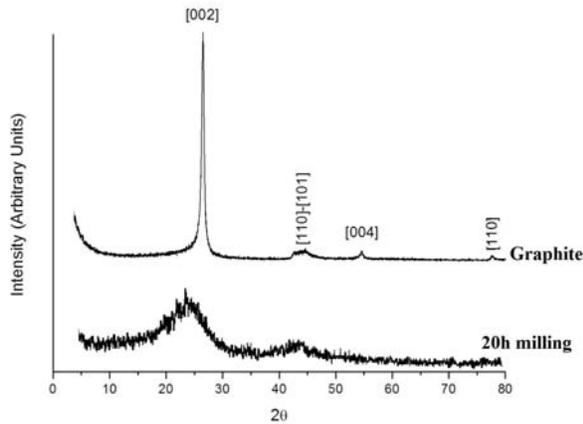


Fig. 2. XRD pattern of unground and 20h milled graphite.

After nano hematite and nano amorphous carbon production, these nano powders were mixed and pelleted. And then, pellets were annealed at 800, 900 and 1000 °C. Fig. 3 shows the XRD pattern of annealed samples.

Sample annealed at 800 °C has different peaks than the other samples which annealed at 900 and 1000 °C. Results taken from XRD that the Fe₃C was formed in the sample which annealed at 800 °C

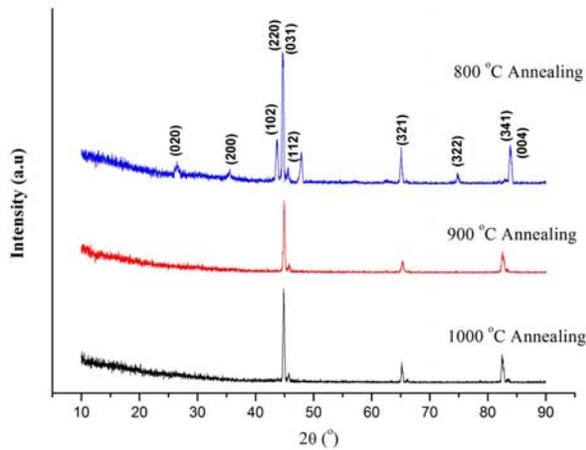


Fig. 3. XRD pattern of samples after annealing process.

Fig. 4 shows the FESEM and WDX analysis of annealed samples at 800 and 1000 °C.

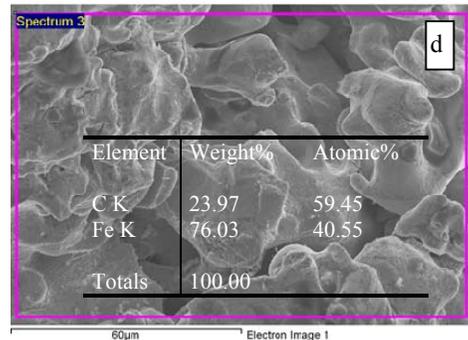
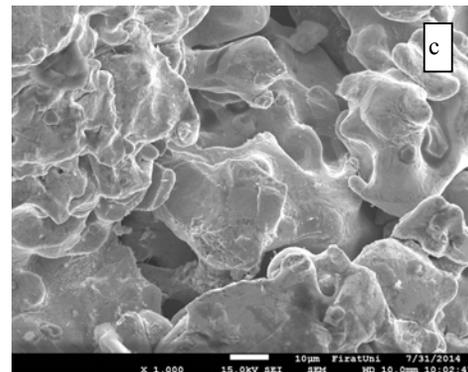
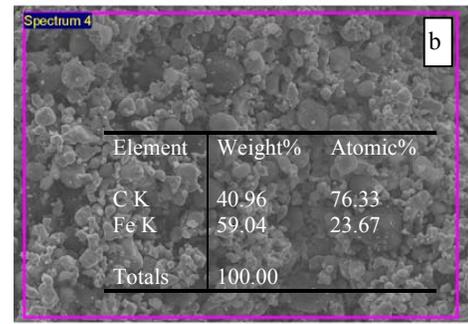
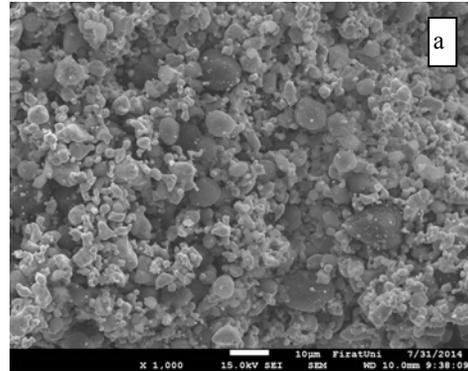


Fig. 4a,b,c,d. FESEM and WDX analysis of annealed samples at a, b) 800 °C, c, d) 1000 °C.

It was seen from Fig. 4a,b that the sample which annealed at 800 °C has a particle structure. But, the sample in Fig. 4c, d which annealed at 1000 °C melts during annealing process. Although 1000 °C annealing temperature is a low temperature for melting, milling

process increases the internal energy of powders and so decreases melting point of powders.

3.1. Second route

In this experiment, hexagonal graphite and commercial iron oxide were used as the starting materials. Graphite and hematite powders were mixed as stoichiometric rate and were milled for 20 hours in inert atmosphere. During milling process, XRD analysis were applied to samples for 10, 15, and 20 h. This XRD analysis were shown in Fig. 5.

Fig. 5 shows that peak intensity were decreased by increasing milling time. But, no full amorphisation occurred after 20 h milling. Partially, graphite peak intensity decreased after 20 h milling. The structure does not transform to amorphous cause of insufficient milling time, especially (002) graphite peak can be still seen in Fig. 5 for each milling times .

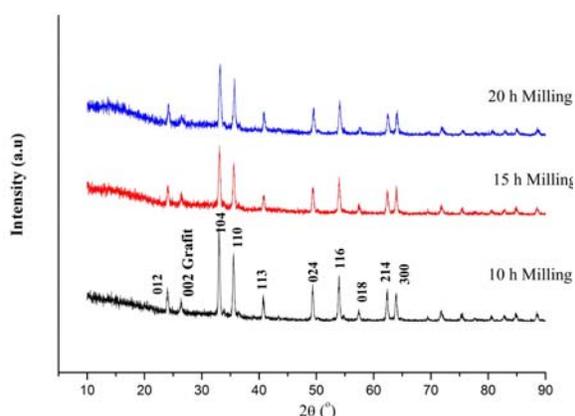


Fig 5. XRD analysis of milled together of hexagonal graphite and commercial iron oxide

After commercial hematite and graphite powders were mixed, these powders were milled for 20 h together and pelleted. And then, pellets were annealed at 800, 900 and 1000 °C. Fig. 6 shows the XRD analysis of annealed samples.

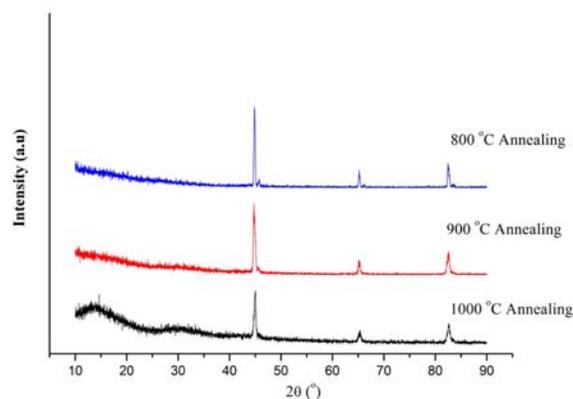


Fig. 6. XRD patterns of samples after annealing process.

In Fig. 6, increased annealing temperature caused a decrease at the peak intensity level. Higher intensity level was obtained from annealed sample at 800 °C.

Fig. 7 shows the FESEM and WDX analysis of milled and then annealed samples at 800 and 1000 °C.

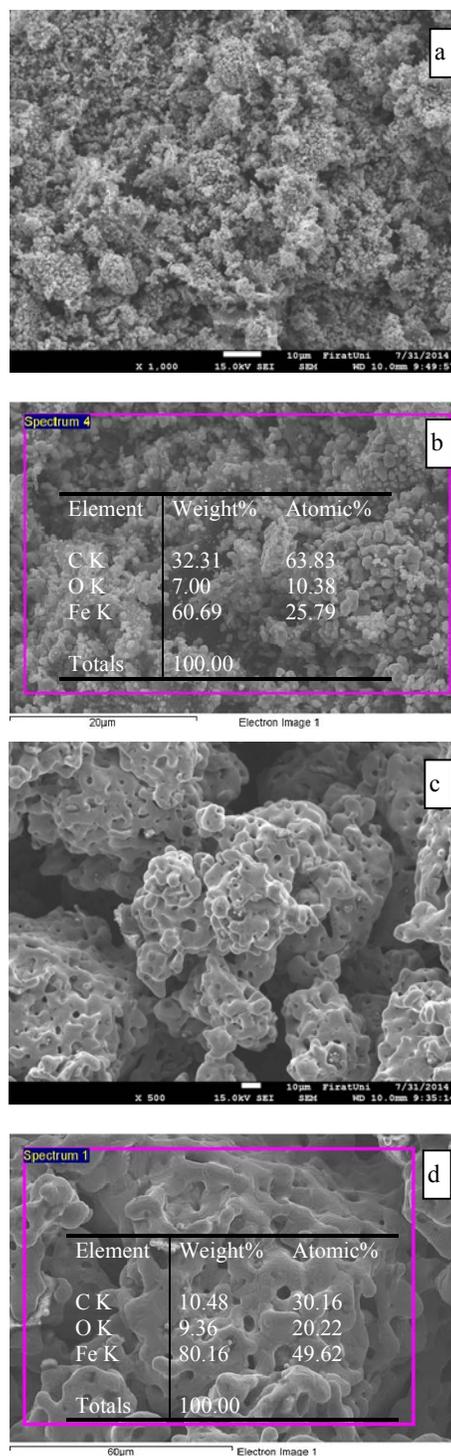


Fig. 7. FESEM and WDX analysis of annealed samples a, b) 800 °C, c, d) 1000 °C

In route one ultra-active nano was converted to amorphous carbon by milling of graphite powder. Besides, the process used for the production of nano hematite increased its reaction capability [8]. Because, the hematite produced in this study had a quite porous structure. By these reasons, annealing process of the powder mixture at 800 °C enabled the cementite formation. FESEM analysis showed that, the cementite formation was not existed in the structure when the annealing temperature was increased and yet more melting occurred although the annealing temperature was below the melting point. The milling process used for the production of the powders increased the internal energy of the powders. Consequently, transition to the liquid phase occurred at the lower temperatures. The reduced carbon and hematite particle size increased the surface areas and therefore the reaction rate. In addition, increasing the process temperature accelerates the reduction which enables carbide formation. Since the process is carburization, melting point of iron decreases. This is one of the reasons of the melting of the sample annealed at temperatures higher than 800 °C [6].

In route two, commercial hematite and graphite powders are milled together for 20 hours. After the milling process XRD results show that the magnitude of the graphite and hematite peaks decreases with the increasing milling time. However, hematite peaks still exist after the 20 hours milling process. It was seen that no cementite was existed in the structure after the annealing process conducted at 800, 900 and 1000 °C following the milling process. This result can be attributed to the insufficient milling time.

Because, the graphite powder mixed with hematite reduced the effectiveness of the milling process due to the lubricating effect of graphite. Full amorphization of graphite after milling was not obtained and non-amorphized graphite prevented both the milling of hematite and the transformation to cementite [9].

In the previous studies it was stated that formation temperature of iron carbide was between 500 and 700 °C [10-12]. Even, it was seen that decomposition rate was higher than the formation rate over 725 °C [11]. In these studies, pure iron was used for Fe₃C formation and hydrocarbon gases or aromatic hydrocarbon were used as the source of carbon. Using both pure iron and carbon sources which have low decomposition temperatures enabled the formation of iron carbide at relatively lower temperatures. In our study, hematite is used for producing iron carbide and this necessitated annealing process at relatively high temperatures.

Because hematite should be reduced to pure iron before the formation of iron carbide. The temperature needed for this reduction process is much higher than the temperature required for the formation of iron carbide. By means of the milling process in this study, the big difference between the reduction temperature of Fe₂O₃ and the formation temperature of Fe₃C is reduced and the reduction temperature of Fe₂O₃ is lowered to a relatively low temperature of 800 °C.

4. Conclusion

Although 800°C is a low temperature both for the reduction of hematite and the formation of iron carbide, iron carbide formation is observed at the samples produced by route one at 800 °C and it is determined that no iron carbide is formed at the annealing processes conducted at higher temperatures. An iron carbide formation at route two samples is not observed for any annealing condition and this is thought to be due to the insufficient milling time.

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*Corresponding author:ertanevin@gmail.com