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The effect of heat treatment and re-calcination on magnetic properties of $BaFe_{12}O_{19}/Fe_3O_4$ nano-composite

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Abstract

In this study a mixture of barium hexaferrite ($BaFe_{12}O_{19}$) and graphite was subjected to intensive milling in a planetary ball mill in order to synthesize $BaFe_{12}O_{19}/Fe_3O_4$ magnetic nano-composite. The effects of milling time and post-synthesis heat treatment on the powder characteristics were investigated using XRD, VSM and HRTEM techniques. XRD results showed that barium hexaferrite partially reduced during high-energy ball milling and nano-composite of $BaFe_{12}O_{19}/Fe_3O_4$ was obtained after 15 h milling of the initial mixture. Analysis of the 40 h milled and then heat-treated samples revealed that reduction of iron oxides proceeded at temperatures above 650 °C. The most intensive peaks of α-Fe were observed in XRD patterns of the samples heat treated at 850 and 950 °C. Magnetic property measurements showed that saturation magnetization of the milled sample increased considerably and coercivity decreased by heat treating at 950 °C. Re-calcination of the aforementioned sample resulted in an increase in coercivity value to 3444.62 Oe. HRTEM image showed nano-crystalline Fe_3O_4 in the structure of 40 h milled sample.

Keywords: A. Milling; B. Nanocomposites; C. Magnetic properties; D. Ferrites

1. Introduction

Barium hexaferrite ($BaFe_{12}O_{19}$) has found wide application as permanent magnet. Other applications of this material are in recording media, microwave filters and magneto-optic materials. The high demand for barium hexaferrite is due to its low cost, high magnetic anisotropy and superior corrosion resistivity [1,2].

Several methods such as co-precipitation, sol–gel combustion and micro-emulsion have been employed to process ultra-fine particles of barium hexaferrite [3–5].

Heat treatment and re-calcination processes have been used to alter magnetic properties of barium or strontium hexaferrites. It is showed that heat treatment of these materials under gases such as nitrogen, hydrogen and carbon-containing gases changes the magnetic properties toward the characteristics of soft magnets. Re-calcination of the heat treated powder results in an increase in the coercivity without considerable decrease in saturation magnetization which is a disadvantage of the chemical processes such as substituting aluminium and chromium in hexaferrites [6–9].

Mechanical milling results in an increase in the reaction kinetics of the reduction reactions. The repeated fracturing and welding of powder particles during milling increases the contact between fresh surfaces. Increments of these contacts, reduction of particle size and storage of strain energy in particles are the most important reasons for increasing the kinetics of reactions and lowering the reaction temperature [10]. Mechanical milling also is a promising technique for producing wide range of nanostructures and magnetic nano-composites [11–15].

The goal of this research was to replace the heat treatment process under carbon containing gases with a novel mechano-chemical technique. It was expected that a new magnetic composite of $BaFe_{12}O_{19}/Fe_3O_4$ owing the desired magnetic properties forms by partial reduction of barium hexaferrite. The

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magnetic properties could also be altered by subsequent heat treatment and post-heat treatment re-calcination processes to produce various compositions of soft/hard magnetic nano-composites.

2. Experimental procedure

Mixture of barium hexaferrite (Sigma–Aldrich, particle size ≤44 μm) and graphite (Sigma–Aldrich, particle size ≤20 μm) was milled in a high-energy ball mill under N_2 atmosphere for different times. The molar ratio of graphite and barium hexaferrite was considered so that C:O molar ratio was 1.1 in the mixture. The rotating speed and ball to powder mass ratio during ball milling were 300 rpm and 35, respectively. The 40 h milled sample was heat treated under vacuum in a tube furnace at different temperatures for 10 min. The 40 h milled and heat treated sample at 950 °C was calcined at 1100 °C for 90 min. The phase composition of the samples was investigated by Bruker D8 advance diffractometer with Co Kα radiation. Crystallite size and structural micro-strains of the milled and heat treated powders were calculated via Williamson–Hall method [16]. Magnetic properties were measured by a LakeShore Model 7307 vibrating sample magnetometer (VSM). Structural investigations were performed with a monochromated FEI Tecnai F20ST/STEM-FEG transmission electron microscope.

3. Results and discussion

Fig. 1 shows the XRD patterns of barium hexaferrite as well a mixture of barium hexaferrite and graphite milled for different times. Fe_3O_4 phase starts to form in the sample milled for 15 h due to the partial reduction of $BaFe_{12}O_{19}$ phase. In 20 and 40 h milled samples, the proportion of Fe_3O_4 has been increased and a magnetic nano-composite of $BaFe_{12}O_{19}/Fe_3O_4$ has been formed. $Fe_{1-x}O$ peaks can also be seen in the XRD pattern of 40 h milled sample. Table 1 represents the variation of calculated mean crystallite size of barium hexaferrite as a function of milling time as well as induced structural micro-strain due to the milling. It is observed that, mean crystallite size decreases and structural micro-strain increases by increasing milling time.

It has been reported that following reactions can take place in the reduction process of Fe_2O_3 to Fe_3O_4 [17]:

$$3Fe_2O_3(s) + C(s) = 2Fe_3O_4(s) + CO(g), \quad \Delta H > 0 \qquad (1)$$

$$3Fe_2O_3(s) + CO(g) = 2Fe_3O_4(s) + CO_2(g), \quad \Delta H < 0 \qquad (2)$$

The energy required for direct reduction with carbon in solid state (reaction (1)) is provided by the impact energy of the balls during mechanical milling. The increased local temperature and pressure as well as producing fresh surfaces due to the fracture of particles in mechanical milling facilitate the reaction (1). The reduction of Fe_2O_3 with graphite, to lower iron oxides in mechanical milling medium has been reported earlier [18,19]. The graphite becomes amorphous by preceding the

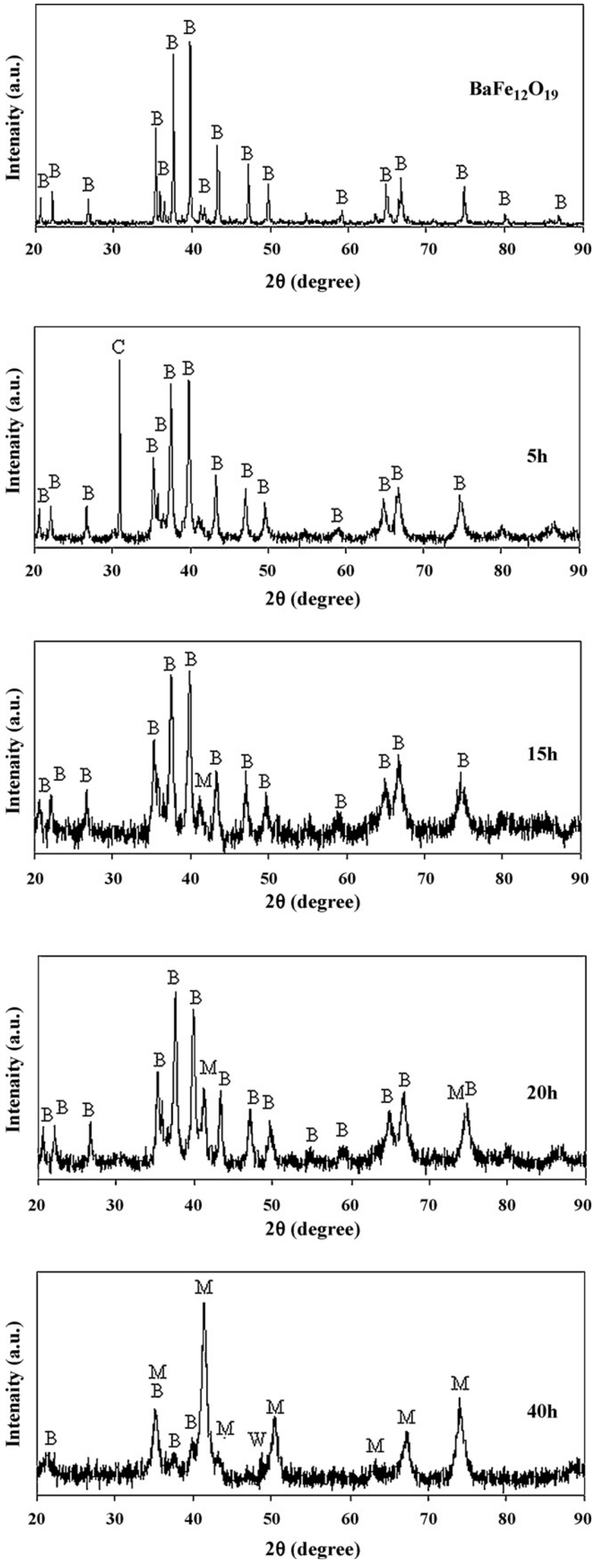

Fig. 1. XRD patterns of barium hexaferrite and a mixture of barium hexaferrite and graphite milled for different times: 5, 15, 20 and 40 h; B = $BaFe_{12}O_{19}$, M = Fe_3O_4, W = $Fe_{1-x}O$ and C = C.

Table 1
Mean crystallite size of barium hexaferrite and structural micro-strain in the samples milled for different times.

Milling time (h)	Mean crystallite size (nm)	Structural micro-strain
5	82	0.43
15	54	1.12
20	37	1.36
40	10	1.45

milling process. This phenomenon has been reported in the previous works [20].

Nano-crystallites of Fe_3O_4 with a mean crystallite size of 10 nm can be observed in the HRTEM image of 40 h milled sample (Fig. 2). Comparison of the calculated lattice plane distances (*d*) with that of the possible phases, i.e. $BaFe_{12}O_{19}$, Fe_2O_3 and Fe_3O_4 confirms the existence of Fe_3O_4 phase as a result of partial reduction of $BaFe_{12}O_{19}$ during the mechano-chemical process.

XRD patterns of the 40 h milled and heat treated samples are presented in Fig. 3. Phase constitutions of the heat treated samples at various temperatures are summarized in Table 2. Analysis of the XRD patterns revealed that in the sample heat treated at 450 °C considerable progress in the reduction process does not occur. However, in the sample heat treated at 650 °C, the intensity of $Fe_{1-x}O$ peaks were increased which is an evident for further progress of reduction process. α-Fe as a dominant phase together with some intermediate phases and remained carbon is detected in the XRD patterns of the samples heat treated at 850 and 950 °C. It seems that the remained amorphous carbon in the milled samples crystallized in the heat treated samples.

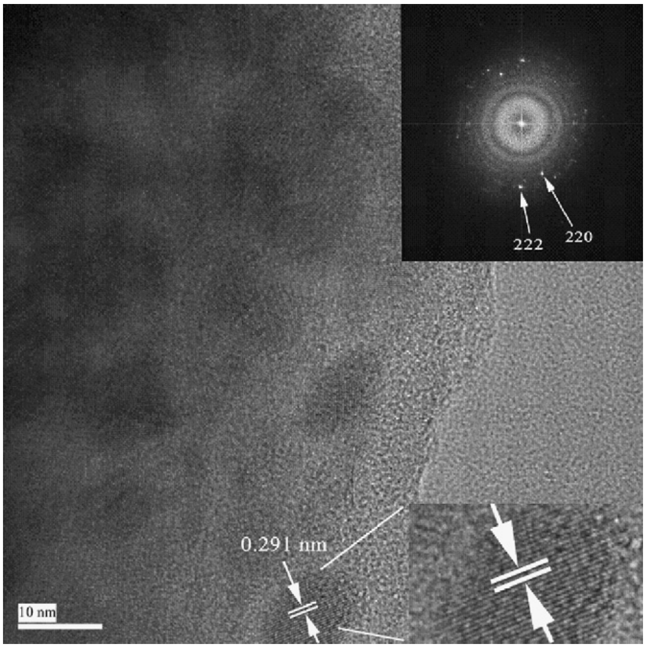

Fig. 2. HRTEM image of 40 h milled samples: inset in the top right is the Fast Fourier Transform of the image in which spots of crystallographic planes of Fe_3O_4 are indicated.

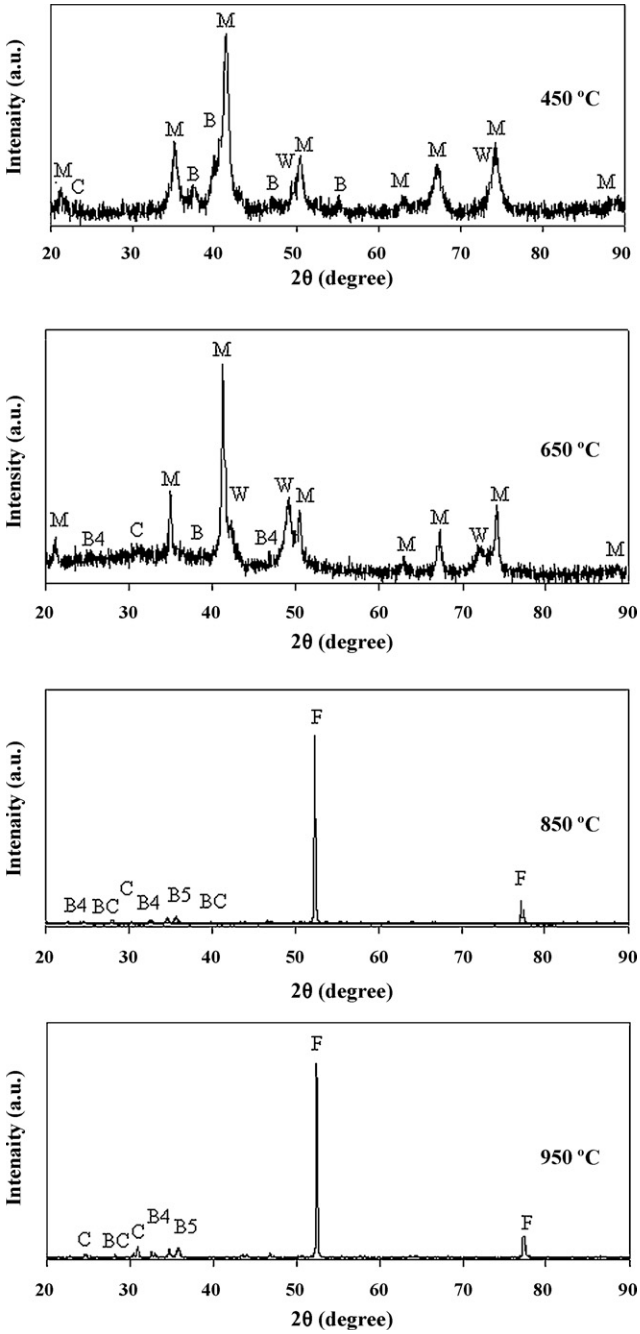

Fig. 3. XRD patterns of 40 h milled sample heat treated at different temperatures for 10 min: B = $BaFe_{12}O_{19}$, M = Fe_3O_4, W = $Fe_{1-x}O$, C = C, B4 = $BaFe_2O_4$, B5 = $Ba_2Fe_2O_5$, BC = $BaCO_3$ and F = α-Fe.

Table 2
Phases which are detected in XRD patterns of 40 h milled samples after heat treatment at different temperatures.

Temperature (°C)	Phases
450	Fe_3O_4, $BaFe_{12}O_{19}$, $Fe_{1-x}O$
650	Fe_3O_4, $BaFe_{12}O_{19}$, $Fe_{1-x}O$, C, $BaFe_2O_4$
850	$BaFe_2O_4$, $Ba_2Fe_2O_5$, Fe, C, $BaCO_3$
950	$BaFe_2O_4$, $Ba_2Fe_2O_5$, Fe, C, $BaCO_3$

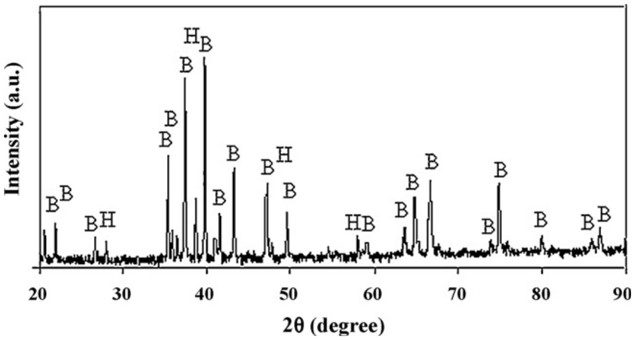

Fig. 4. XRD pattern of the 40 h milled sample, heat treated at 950 °C and then re-calcined at 1100 °C for 90 min: B = $BaFe_{12}O_{19}$ and H = α-Fe_2O_3.

XRD pattern of the 40 h milled sample after heat treating at 950 °C for 10 min and re-calcination at 1100 °C for 90 min shows the existence of barium hexaferrite as a major phase together with small amount of α-Fe_2O_3 in this sample (Fig. 4). It seems that the barium hexaferrite recovers during the re-calcination process.

Fig. 5 exhibits hysteresis loops of as-received barium hexaferrite powder, 40 h milled, 40 h milled and heat treated at 950 °C sample and aforementioned sample after re-calcination at 1100 °C for 90 min. Coercivity and saturation magnetization of barium hexaferrite reduce by 40 h of milling from 2028.54 to 201.80 Oe and from 64.75 to 38.12 emu/g, respectively. This is due to the existence of graphite as a diluents as well as formation of Fe_3O_4 soft magnetic phase. Induced strain during high-energy ball milling (see Table 1) can also demolish the magnetic properties. The induced structural micro-strains of the 40 h milled sample decreases from 1.45 to 0.19 after vacuum heat treatment at 950 °C and to 0.10 after re-calcination. The released strains in the heat-treated samples might have an influence in the recovery of the magnetic properties.

Formation of iron as a result of heat treatment of milled sample results in a strong increase in the saturation magnetization to 168.74 emu/g and decrease in the coercivity to 18.78 Oe which both are characteristics of soft magnetic materials. Indeed, milling of barium hexaferrite with graphite and subsequent heat treatment converts barium hexaferrite hard magnetic material to a soft one. Due to presence of some intermediate phases like $BaFe_2O_4$, $Ba_2Fe_2O_5$, $BaCO_3$ and also remained carbon, the saturation magnetization is smaller than that of pure iron.

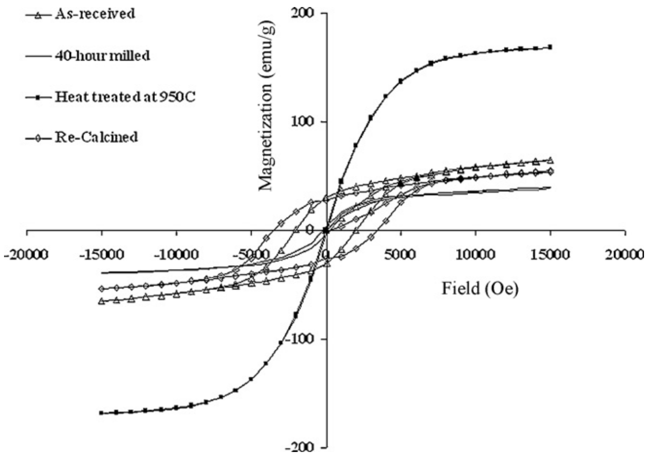

Fig. 5. Hysteresis loops of as-received barium hexaferrite, 40 h milled powder mixture, 40 h milled and heat treated at 950 °C and re-calcined sample at 1100 °C.

Re-calcination of the milled and heat treated powder increases the coercivity to 3444.62 Oe and decreases the saturation magnetization to 53.56 emu/g. The increase in coercivity might be due to the refinement of the particle size in the sample. The decrease in saturation magnetization compared to initial barium hexaferrite could be due to the presence of small amount of Fe_2O_3 in the re-calcined sample.

4. Conclusions

Barium hexaferrite was mixed with graphite and treated mechano-chemically in a high energy ball mill. Some samples were heat treated and then re-calcined. Accordingly, following conclusions were drawn:

1. Ball milling of barium hexaferrite and graphite led to reduction of $BaFe_{12}O_{19}$ to Fe_3O_4 after 15 h of milling. The Fe_3O_4 phase was the dominant phase in the 40 h milled sample.
2. Heat treatment of the 40 h milled sample at temperatures above 650 °C resulted in the progress of the reduction process which was started in the milling stage. α-Fe was formed together with Ba containing phases and remained carbon by increasing heat treatment temperature to 850 °C.
3. The magnetic properties were demolished due to the milling process. Heat treatment of the 40 h milled sample at 950 °C resulted in a considerable increase in saturation magnetization.
4. Re-calcination of the heat-treated sample resulted in the recovery of barium hexaferrite compound and hence increasing the coercivity value to 3444.62 Oe.

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References

[1] P. Campbell, Permanent Magnet Materials and Their Application, Cambridge University Press, Cambridge, 1994.
[2] U. Topal, H. Ozkan, H. Sozeri, Synthesis and characterization of nanocrystalline $BaFe_{12}O_{19}$ obtained at 850 °C by using ammonium nitrate melt, J. Magn. Magn. Mater. 284 (2004) 416–422.
[3] V. Pillai, P. Kumar, D.O. Shah, Magnetic properties of barium ferrite synthesized using a microemulsion mediated process, J. Magn. Magn. Mater. 116 (1992) L299–L304.
[4] L. Junliang, Z. Yanwei, G. Cuijing, Z. Wei, Y. Xiaowei, One-step synthesis of barium hexaferrite nano-powders via microwave-assisted sol–gel auto-combustion, J. Eur. Ceram. Soc. 30 (4) (2010) 993–997.

[5] M.M. Rashad, M. Radwan, M.M. Hessien, Effect of Fe/Ba mole ratios and surface active agents on the formation and magnetic properties of co-precipitated barium hexaferrite, J. Alloy Compd. 453 (2008) 304–308.

[6] A. Ataie, I.R. Harris, C.B. Ponton, Hexaferrite materials, U.S. Patent 5,858,265, 1999.

[7] A. Ataie, C.B. Ponton, I.R. Harris, Heat treatment of strontium hexaferrite powder in nitrogen, hydrogen and carbon atmospheres: a novel method of changing the magnetic properties, J. Mater. Sci. 31 (1996) 5521–5527.

[8] S.A. Seyyed Ebrahimi, A. Kianvash, C.B. Ponton, I.R. Harris, The effect of hydrogen on composition, microstructure and magnetic properties of strontium hexaferrite, Ceram. Int. 26 (2000) 379–381.

[9] M.M. Hessien, M. Radwan, M.M. Rashad, Enhancement of magnetic properties for the barium hexaferrite prepared through ceramic route, J. Anal. Appl. Pyrol. 78 (2007) 282–287.

[10] C. Suryanarayana, Mechanical alloying and milling, Prog. Mater. Sci. 46 (2001) 1–184.

[11] N.H. Vasoya, L.H. Vanpariya, P.N. Sakariya, M.D. Timbadiya, T.K. Pathak, V.K. Lakhani, K.B. Modi, Synthesis of nanostructured material by mechanical milling and study on structural property modifications in $Ni_{0.5}Zn_{0.5}Fe_2O_4$, Ceram. Int. 36 (3) (2010) 947–954.

[12] R. Arbain, M. Othman, S. Palaniandy, Preparation of iron oxide nanoparticles by mechanical milling, Miner. Eng. 24 (1) (2011) 1–9.

[13] X.Y. Qin, R. Cao, H.Q. Li, Fabrication and mechanical properties of ultrafine grained γ-Ni–20Fe/Al_2O_3 composites, Ceram. Int. 32 (5) (2006) 575–581.

[14] S. Bid, S.K. Pradhan, Preparation of zinc ferrite by high-energy ball-milling and microstructure characterization by Rietveld's analysis, Mater. Chem. Phys. 82 (1) (2003) 27–37.

[15] E.P. Yelsukov, G.A. Dorofeev, A.I. Ulyanov, A.V. Zagainov, A.N. Maratkanova, Mossbauer and magnetic study of nanocrystalline Fe obtained by mechanical milling in argon, Phys. Met. Metallogr. 91 (2001) 1–8.

[16] G.K. Williamson, W.H. Hall, X-ray line broadening from filed aluminium and Wolfram, Acta Metall. 1 (1) (1953) 22–31.

[17] Y. Kashiwaya, H. Suzuki, K. Ishii, Gas evolution during mechanical milling of hematite–graphite mixture, ISIJ Int. 44 (12) (2004) 1970–1974.

[18] C.H. Lee, S.H. Lee, S.Y. Chun, S.J. Lee, J.S. Kim, Mechanical alloying effect of hematite and graphite, Mater. Sci. Forum. 449–452 (2004) 257–260.

[19] M. Zdujić, C. Jovalekić, Lj. Karanović, M. Mitrić, The ball milling induced transformation of α-Fe_2O_3 powder in air and oxygen atmosphere, Mater. Sci. Eng. B 262 (1999) 204–213.

[20] T. Tanaka, M. Motoyama, K.N. Ishihara, P.H. Shingu, Characterization of carbon in mechanically alloyed C–10 at%Fe powder, Mater. Trans. JIM 36 (1995) 276–281.