Journal of Alloys and Compounds 489 (2010) 269–274

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

In situ synthesis of high density magnetic ferrite spinel ($MgFe_2O_4$) compacts using a mixture of conventional raw materials and waste iron oxide

Y.M.Z. Ahmed*, E.M.M. Ewais, Z.I. Zaki

Central Metallurgical Research and Development Institute (CMRDI), P.O. Box 87 Helwan, Cairo 11421, Egypt

ARTICLE INFO

Article history:
Received 5 May 2009
Received in revised form
14 September 2009
Accepted 15 September 2009
Available online 23 September 2009

Keywords:
Magnesium ferrite
Magnetic properties
Saturation magnetization
Coercivity
Compressive strength

ABSTRACT

A mixture of magnesite ore and waste iron oxide (mill scale) was used to synthesize high density magnesium ferrite compacts. The effect of different mixture composition (weight percentage of magnesite ore to mill scale) as well as the sintering temperatures on the phase change, compressive strength, physical and magnetic properties of sintered compacts was investigated. The results indicated that a single phase ferrite spinel is obtained in a compact produced from a mixture consisting of 40 wt% magnesite ore and 60 wt% mill scale and sintered at different temperatures. On the other hand, this mixture composition produced compacts possessing low porosity and high saturation magnetization of 6% and 31.89 emu/g, respectively when it is sintered at 1550 °C for 2 h.

1. Introduction

Spinel ferrites with the general formula AB_2O_4 (A = Mn, Mg, Co and Ni) are very important magnetic materials because of their interesting magnetic properties combined with chemical and thermal stability [1]. Magnesium ferrite, $MgFe_2O_4$ is regarded as an important candidate of the spinel family. It has a cubic structure of the normal spinel-type and is a soft magnetic n-type semiconducting material, which finds a wide number of applications in heterogeneous catalysis [2–5], gas sensors [6,7], transformers, ferrofluids and magnet core of coils [3,8–11]. It has been demonstrated that this material can be used for thermal coagulation therapy, in which tumors are locally heated by application of an alternating magnetic field [12]. The general formula of magnesium ferrite, $MgFe_2O_4$, could be written as $(Mg_{1-x}Fe_x)[Mg_xFe_{2-x}]O_4$, where parentheses and square brackets denote cation sites of tetrahedral (A) and octahedral [B] coordination, respectively. The subscript letter x represents the so-called degree of inversion (defined as the fraction of the (A) sites occupied by Fe^{3+} cations). It is widely appreciated that properties of $MgFe_2O_4$ are highly sensitive to both the cation distribution and the spin configuration which in turn depend on the route of synthesis of the material.

Several methods for synthesizing magnesium ferrites were found in the literature including coprecipitation [13], a supercritical drying processes [3,9], a micelle route [11], hydrothermal synthesis [14,15], and a solid state reaction [6,7,16]. The most conventional and economical method for preparation of magnesium ferrite is the solid state reaction [13]. In this method the spinel is synthesized by the chemical reaction between mixed oxides, hydroxides or carbonates at high temperature, where the reaction product is formed by the thermal diffusion of cations through the ferrite film formed between the starting oxides. In general, pure oxides, hydroxide and carbonates were used as starting materials in synthesizing most of the ferrites using this technique.

Here, a trial is made of using a solid state reaction technique for synthesizing high density magnesium ferrite from a mixture of conventional raw materials (Egyptian magnesite ore) and waste iron oxide material (mill scale). Mill scale is considered as a valuable secondary raw material as a result of its high iron content, low impurities and stable chemical composition. This material is produced in huge quantities in steel making plants during the heating and subsequent rolling of steel slabs. Its specific production is about 35–40 kg/ton of hot rolled product. Thus, for a million ton-a-year steel plant, 35,000–40,000 tons of mill scale is produced. This amount of mill scale contains about 25,000–30,000 tons iron. On the other hand, magnesite ore located in high reserves in the Eastern desert in Egypt mainly consists of magnesium carbonate ($MgCO_3$) with traces of other impurities (such as: CaO, K_2O, Na_2O, SiO_2 and Al_2O_3). This material could be regarded as an excellent source of MgO. Accordingly, both mentioned materials (mill scale and mag-

---

* Corresponding author at: Central Metallurgical Research and Development Institute (CMRDI), Advanced Materials, P.O. Box 87 Helwan, Cairo 11421, Egypt. Tel.: +20 2 25516462; fax: +20 2 25010639.
E-mail address: ahmedymz@hotmail.com (Y.M.Z. Ahmed).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.09.069

Table 1
Chemical composition of non-standard raw materials.

Composition (%)	Egyptian magnesite ore	Mill scale
Fe_{total}	0.042	74.2
Fe_{metal}	–	4
FeO	–	39.4
Fe_3O_4	0.06	30.77
SiO_2	0.88	0.36
Al_2O_3	0.53	0.14
CaO	4.42	0.18
MgO	42.71	0.13
S	–	0.022
Na_2O	0.24	–
K_2O	0.1	–
L.O.I.[a]	50.26	0.65
C	–	0.65

[a] Loss of ignition.

nesite ore) could be an excellent candidate in synthesizing a variety of both hard and soft ferrites especially magnesium ferrite spinel.

In commercial technologies where ferrites are used as a rule, materials of high density are required. Thus, magnesium ferrites are often prepared from finely ground and highly reactive precursor powders that, at high temperatures, are densified by sintering through solid state reactions.

Meanwhile, using secondary resources or waste materials can bring a higher output of ferrite at lower cost and make a break-through in raw materials as well as technology. So it can be considered as an economically valuable and environmental-friendly process. Here, a ceramic method was applied to investigate the effect of both sintering temperature and mixture composition (weight ratio of magnesite ore to mill scale) on the phase formation during sintering as well as the physical, mechanical and magnetic properties of the sintered sample.

2. Experimental procedure

A mill scale sample was obtained from the Egyptian Iron and Steel Company, while the magnesite ore was delivered from the Eastern desert, Egypt. The total chemical composition of both materials is given in Table 1. Both materials were finely ground to a mean particle size of 74 μm. Various batches of different mixture composition from both materials were thoroughly mixed. The composition of the mixtures is designed on the basis of increasing mill scale amount at the expense of magnesite ore. The mixture composition is varied from 40 wt% magnesite ore with 60 wt% mill scale to 10 wt% magnesite ore with 90 wt% mill scale. The mixed samples were pressed into compacts of a nominal diameter 13 and 18 mm height using a uniaxial press machine. The green compacts produced were dried at 105 °C for 24 h, and then treated at different temperatures. The synthesis temperature of pure $MgFe_2O_4$ using conventional solid state reaction is higher than 1300 °C [17]. Accordingly, various sintering temperatures varying from 1300 to 1550 °C were applied for the dried compacts. The bulk density as well as apparent porosity of the sintered compacts was evaluated using Archimedes method. The compressive strength was measured at ambient temperature using a universal test machine at a strain rate of $9.26 \times 10^{-4}\,s^{-1}$. The different phases formed at different firing temperatures were identified by the X-ray diffraction (XRD) technique (PW 1730) with nickel-filtered Cu radiation ($\lambda = 1.5$ Å) at 40 kV and 30 mA. On the other hand, the microstructural changes accompanying the heat treatment of the compacted mixtures were examined by a scanning electron microscope (JEOL-JSM-5410) equipped with electron dispersive X-ray spectrometer unit. The magnetic properties of the samples produced were studied using the vibrating sample magnetometer (model VSM-9600 M-1, USA). The measurements were conducted at room temperature in a maximum applied field of 15 kOe. From the hysteresis loops obtained the magnetic properties were determined.

3. Results and discussion

3.1. Effect of the amount of mill scale

The effect of the amount of mill scale varied from 60 to 90 wt% on the phase changes as well as the physical and magnetic properties of sintered compacts were investigated. The sintering conditions were kept constant at 1300 °C for 2 h. Fig. 1 shows the X-ray diffraction patterns for sintered compacts containing different amounts of mill scale. It is clearly noticed that a spinel structure of magnesium ferrite ($MgFe_2O_4$) which is described in JCPDS # 88-1935 is detected in all samples. Eight peaks centered at $2\theta = 30.3°$, 35.67°, 37.3°, 43.92°, 53.6°, 58.07°, 62.9° and 47.02°, which correspond to diffraction planes of (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 3 4), respectively are detected. According to JCPDS # 88-1935, the phase obtained has a cubic structure whose space group is Fd3m (2 2 7) with a lattice parameter of $a = 9.38$ Å. However, a single phase spinel is obtained only for the sample containing 60 wt% mill scale. At 70 wt% mill scale, other peaks related to hematite phase (Fe_2O_3) (JCPDS # 76-1166) was clearly developed. The intensity of hematite peaks was increased markedly with an increase in the amount of mill scale. For the sample containing 40 wt% magnesite ore with 60 wt% mill scale, the Mg:Fe mole ratio was found to be equal to 1:2.1. This mole ratio is slightly higher than the stoichiometric mole ratio of Mg:Fe (1:2) required for synthesizing magnesium ferrite using a ceramic technique. With an increase in the amount of mill

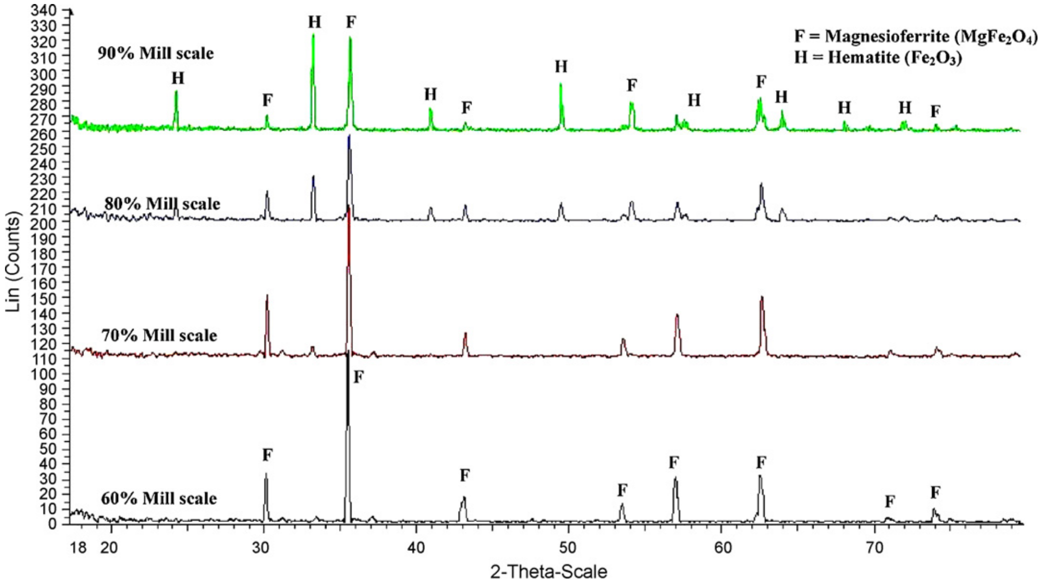

Fig. 1. X-ray patterns for samples containing different amounts of mill scale and sintered at 1300 °C for 2 h.

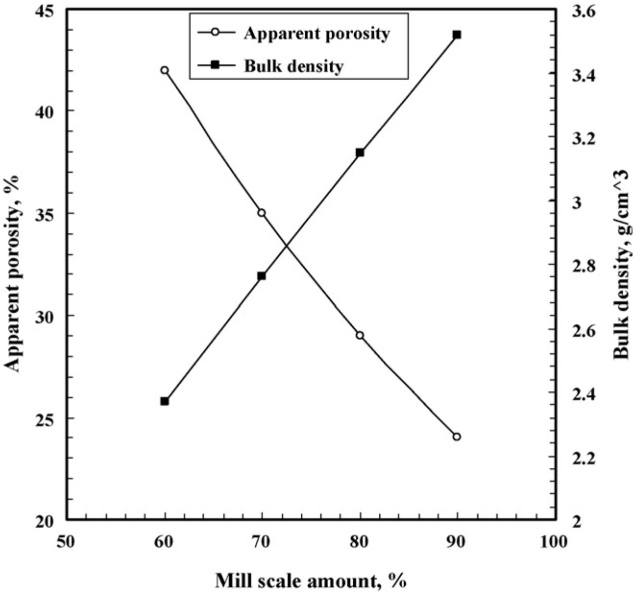

Fig. 2. Effect of the amount of mill scale on the bulk density and apparent porosity of sintered samples.

scale in the compacted sample there was an increase in the free iron oxide (hematite) produced from the oxidation of unreacted mill scale which consists mainly of magnetite (Fe_3O_4) and wustite (FeO).

The effect of the amount of mill scale on the physical properties of the sintered compacts in terms of bulk density and apparent porosity is shown in Fig. 2. It can be seen that increasing the amount of mill scale leads to a significant increase in the bulk density with a sharp decrease in the apparent porosity. This behavior is attributed to the presence of magnetite as a main constituent of mill scale. When pure magnetite is roasted at temperatures above ~815 °C, it oxidized rapidly to hematite with release of large amounts of energy [18]. The oxidation reaction, shown in Eq. (1), is highly exothermic and the amount of energy released from this reaction acts as additional source of heat which supports sintering process [19].

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \quad (1)$$

The increase of the amount of mill scale leads to release of more amounts of heat during its oxidation which consequently boosts the sample sinterability. This observation is confirmed from the scanning electron microscope examination of the sintered compacts shown in Fig. 3. With increasing amount of mill scale from 60 to 90 wt% a considerable increase in the grain size of ferrite spinel takes place from about 1–2 μm to >10 μm, respectively. This grain growth can be related to the excess heat generated from the oxidation of magnetite. However, this growth in the grain size is responsible for an increase in the bulk density and a decrease in the apparent porosity. Also, the increase of the grain size of the spinel formed with increasing amounts of mill scale is due to the fact that with a change in the relative amount of the powders of the starting phases it is possible to vary the number of nucleation centers for the new phase, which affect the crystallite size of the new phase being formed [20]. In case of a mixture of magnesium and iron oxides, the thermal stability of the MgO lattice is much greater than that of Fe_2O_3 lattice [20]. Also, the diffusional mobility of iron cations is higher than that of magnesium cations [20]. Accordingly, the crystal lattice of the spinel phase should form mainly on the basis of the magnesium oxide lattice. Hence, with a decrease in the concentration of magnesium oxide, the crystal lattice which apparently forms the basis of the structure of the ferrite, there is a decrease in the number of nuclei and then an increase of the grain size of the resultant ferrite [20]. In addition, the microstructure of the sintered compacts revealed that the sample containing 60 wt% mill scale contains high porosity percentage with small and large pores. With an increased amount of mill scale, these large pores completely disappeared and only small ones were observed.

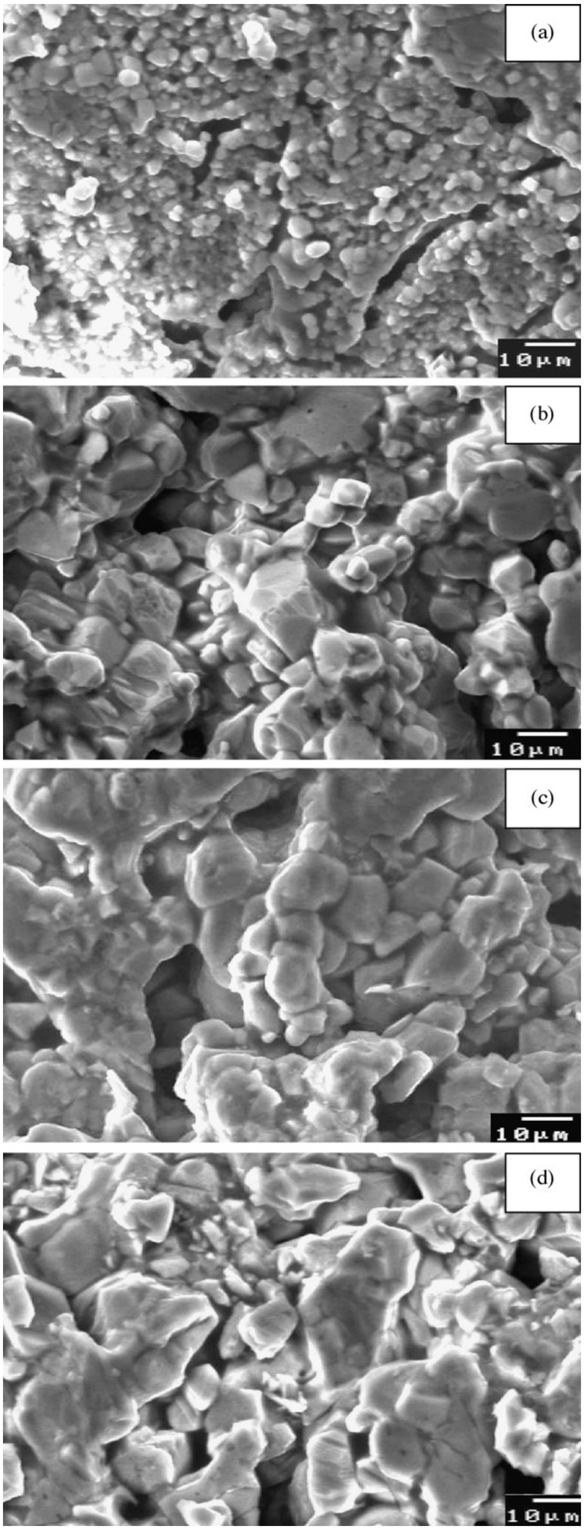

Fig. 3. SEM micrographs of sintered samples containing different percentages of mill scale: (a) 60%, (b) 70%, (c) 80% and (d) 90%.

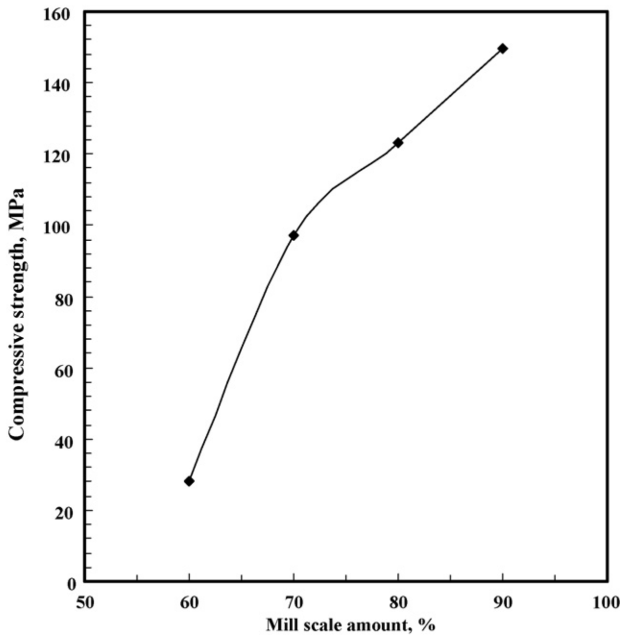

Fig. 4. Effect of the amount of mill scale amount on the compressive strength of sintered samples.

The compressive strength of the sintered compacts as a function of the amount of mill scale is shown in Fig. 4. It is clear that increasing the amount of mill scale leads to a sharp increase in the compressive strength of the sintered compacts. This is attributed to the enhancement in the sinterability with decreasing the apparent porosity.

Fig. 5 shows the hysteresis loops for sintered samples containing different amounts of mill scale, while the magnetic properties of sintered samples in terms of saturation magnetization and coercivity are given in Fig. 6. It is found that by increasing the amount of mill scale from 60 to 70 wt% there is a slight increase in the saturation magnetization with an insignificant increase in the coercivity. A further increase in the amount of mill scale (beyond 70 wt%) leads to a sharp decrease in the saturation magnetization with a large increase in the coercivity. It is believed that the magnetic properties are largely dependent on the sample microstructure as well as its density [21,22]. Increasing the amount of mill scale leads to a considerable increase in the grain size of the spinel formed as well as an increase in the sample density. This fact would be responsible for a sharp increase in the saturation magnetization instead of the slight increase detected. On the other hand, the presence of the hematite species (Fe_2O_3) was found to be responsible for a retardation of the sample magnetic properties [23]. This means that, there are two competing modes one (density and grain size) is responsible for increasing the magnetization, while the other (Fe_2O_3 species) is responsible for retardation of the magnetic properties. These two competing modes may easily account for the slight increase of saturation magnetization with increasing amount of mill scale from 60 to 70 wt%. The presence of traces of Fe_2O_3 species in the 70% sample is responsible for the unexpected slight increase in the magnetization. A further increase in the amount of mill scale results in a large amount of Fe_2O_3 in the sample produced and its effect on the magnetization will predominate leading to a sharp decrease in the saturation magnetization. In addition Fe_2O_3 having a high intrinsic coercive force [24] means that increasing its percentage in the sintered sample is responsible for a large increase in the coercivity.

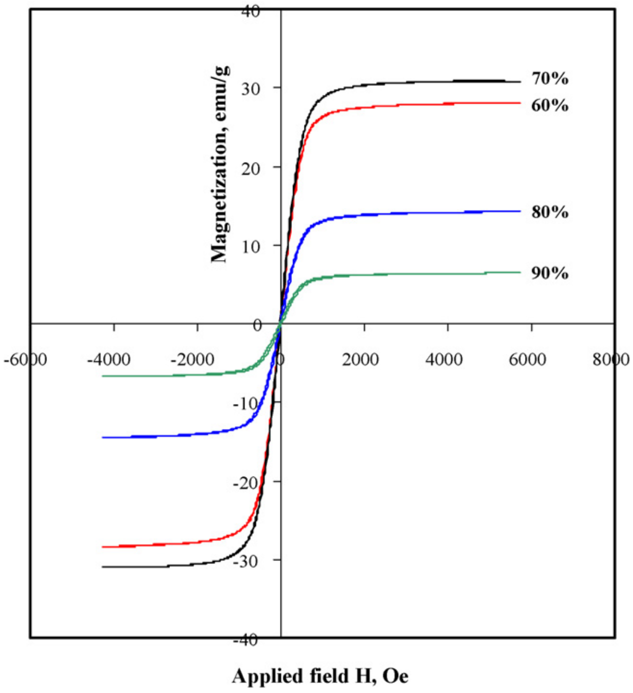

Fig. 5. Magnetization hysteresis for samples containing different amounts of mill scale.

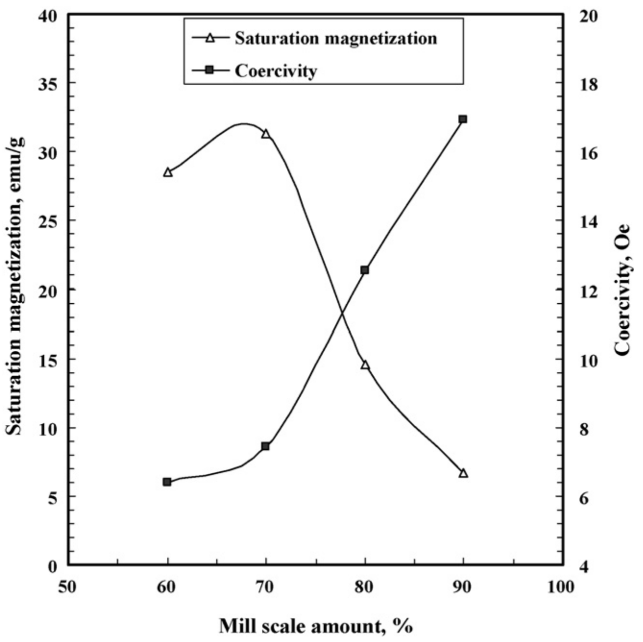

Fig. 6. Effect of the amount of mill scale on the magnetic properties of sintered samples.

The previous study indicates that, although the sample density is improved with increasing mill scale amount it retards the magnetic properties of the final product via introducing much amounts of weak magnetic properties species (Fe_2O_3). Accordingly the increase in sintering temperature for the sample possesses single phase ferrite spinel (40 wt% magnesite ore with 60 wt% mill scale) would be the solution for producing high density compacts of single phase ferrite spinel.

3.2. Effect of sintering temperature

Fig. 7 shows the X-ray diffraction patterns for a sample containing 40 wt% magnesite ore and 60 wt% mill scale and sintered at different temperatures for 2 h. It is revealed that no changes in the

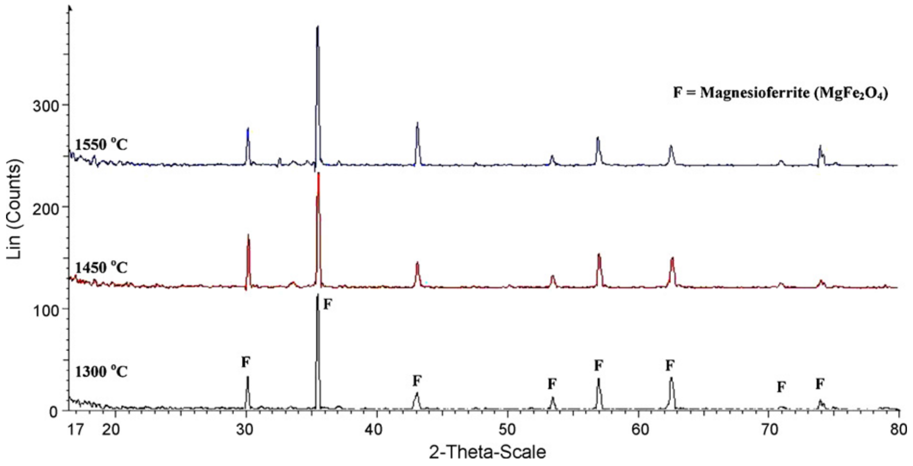

Fig. 7. X-ray diffraction patterns for sample containing 60% mill scale and sintered at different temperatures.

phase composition were observed upon increasing the sintering temperatures up to 1550 °C. Single phase magnesium ferrite phase was obtained for all the sintered samples. This is a good indication of the high thermal stability of the magnesium ferrite phase. It is worth mentioning that for the sample sintered at a much higher temperature (at 1650 °C, not given) a semi fusion occurred in the sintered sample. This is related to the fact that the melting point of magnesium ferrite is about 1760 °C.

The properties of the compacts sintered at different temperatures (bulk density, apparent porosity, compressive strength, saturation magnetization and coercivity) are given in Table 2. It is clear that increasing the sintering temperature leads to a sharp increase in the bulk density and compressive strength while the apparent porosity is sharply decreased. This is attributed to the fact that with increasing sintering temperature the compact sinterability is largely improved. It is well known that the sintering temperature, soaking time and compaction pressure are the main parameters controlling the compact sinterability. Increasing the values of any one of them leads to a large improvement in the compact sinterability [25]. The enhancement in sinterability gives opportunity for the grain boundaries to contact at the expense of the entire porosity, leading to pore-closing and elimination. This interpretation is confirmed with the SEM investigations shown in Fig. 8. The low and high magnification micrographs of samples sintered at 1450 and 1550 °C revealed that increasing the sinter-

Table 2
Effect of sintering temperature on the properties of sintered samples.

Properties	Sintering temperature (°C)		
	1300	1450	1550
Bulk density (g/cm^3)	2.37	3.05	3.71
Apparent porosity (%)	42	25	6
Compressive strength (MPa)	28.24	97.97	125.6
Saturation magnetization (emu/g)	28.56	29.42	31.89
Coercivity (Oe)	6.397	5.524	4.294

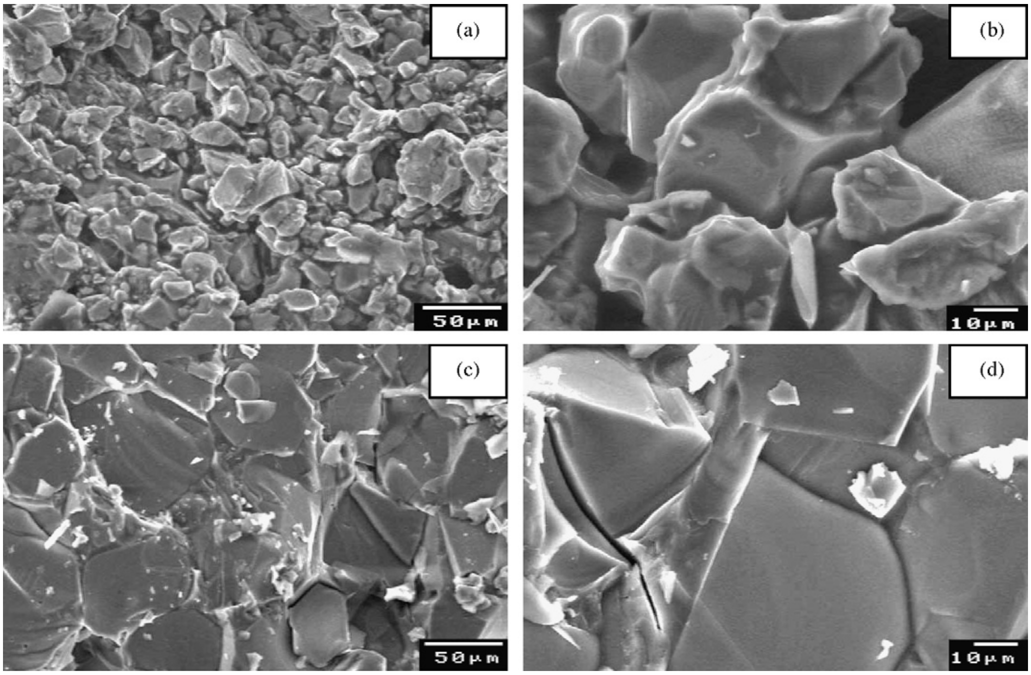

Fig. 8. SEM micrograph of sintered samples containing 60% mill scale and sintered at different temperatures. (a) and (b) low and high magnifications of sample sintered at 1450 °C, respectively. (c) and (d) low and high magnifications of sample sintered at 1550 °C, respectively.

ing temperature leads to a better grain growth at the expense of the total porosity. By increasing the sintering temperature to 1550 °C the grain growth is improved and forms large grain size of about 50 μm. Such effect of sintering temperature (without any remarkable change in the phase formation during sintering) is the main reason for improving the magnetic properties of the sintered compacts. The saturation magnetization is found to be increased with an increase in the sintering temperature while the coercivity decreased. The most important observation here is that a high density single phase magnesium ferrite compact with a porosity of about 6% is obtained for a sample sintered at 1550 °C. In addition, this sample possesses the highest saturation magnetization of 31.89 emu/g which is too close to the value of 33.4 emu/g for bulk $MgFe_2O_4$ [26]. However, a fully dense magnesium ferrite with a porosity <1% was not obtained under these conditions. On the other hand the sintering temperature for obtaining the high density compacts is too high. These lead us to suggest adding sintering aids to obtain fully dense compacts at expected lower temperatures using the same starting materials. A report on this aspect will be the subject of a separate article.

4. Conclusion

High density magnesium ferrite spinel was successfully synthesized from a mixture of Egyptian magnesite ore and mill scale. Increasing the amount of mill scale in the green compact improved the grain growth, the compressive strength as well as the physical properties of the final sintered compacts. However, it dramatically decreased the magnetic properties of the sintered samples. The effect of different sintering temperatures on the sample possessing a single phase magnesium ferrite spinel revealed that a high density magnesium ferrite compact with extremely high saturation magnetization was obtained for a compact sintered at 1550 °C for 2 h.

References

[1] R. Valenzuela, Magnetic Ceramics, Cambridge University Press, Cambridge, 1994.
[2] B.L. Yang, D.S. Cheng, S.B. Lee, Appl. Catal. 70 (1991) 161–173.
[3] R.J. Willey, P. Noirclerc, G. Busca, Chem. Eng. Commun. 123 (1993) 1–16.
[4] C. Xiong, Q. Chen, W. Lu, H. Gao, W. Lu, Z. Gao, Catal. Lett. 69 (2000) 231–236.
[5] Y.H. Lee, G.D. Lee, S.S. Park, S.S. Hong, React. Kinet. Catal. Lett. 84 (2005) 311–317.
[6] G. Gusmano, G. Montesperelli, P. Nunziante, E. Traversa, J. Mater. Sci. 28 (1993) 6195–6198.
[7] Y.L. Liu, Z.M. Liu, Y. Yang, H.F. Yang, G.L. Shen, R.Q. Yu, Sens. Actuators B 107 (2005) 600–604.
[8] Q. Chen, Z.J. Zhang, Appl. Phys. Lett. 73 (1998) 3156–3158.
[9] S.A. Oliver, R.J. Willey, H.H. Hamdeh, G. Oliveri, G. Busca, Scripta Metall. Mater. 33 (1995) 1695–1701.
[10] Q. Chen, A.J. Rondinone, B.C. Chakoumakos, Z.J. Zhang, J. Magn. Magn. Mater. 194 (1999) 1–7.
[11] C. Liu, B. Zou, A.J. Rondinone, Z.J. Zhang, J. Am. Chem. Soc. 122 (2000) 6263–6267.
[12] K. Konishi, T. Maehara, T. Kamimori, H. Aono, T. Naohara, H. Kikkawa, Y. Watanabe, K. Kawachi, J. Magn. Magn. Mater. 272–276 (2004) 2428–2429.
[13] C.P. Liu, M.W. Li, Z. Cui, J.R. Huang, Y.L. Tian, T. Lin, W.B. Mi, J. Mater. Sci. 42 (2007) 6133–6138.
[14] S. Verma, H.S. Potdar, S.K. Date, P.A. Joy, in: O.J. Glembocki, C.E. Hunt (Eds.), Nanoparticles and Nanowire Building Blocks—Synthesis, Processing, Characterization and Theory, Materials Research Society, PA, USA, 2004, p. 8319.
[15] Y.J. Huang, J. Wang, Q.W. Chen, Chin. J. Inorg. Chem. 21 (2005) 697–700.
[16] P.V. Reddy, R. Satyanarayana, T.S. Rao, J. Mater. Sci. Lett. 3 (1984) 847–849.
[17] Y. Huang, Y. Tang, J. Wang, Q. Chen, Mater. Chem. Phys. 97 (2006) 394–397.
[18] P.E. Cavanagh, Autogenous roasting of iron ore, US Patent 5376162 (1994).
[19] S.P.E. Forsmo, S.E. Forsmo, P.O. Samskog, B.M.T. Björkman, Powder Technol. 183 (2008) 247–259.
[20] V.P. Pashchenko, G.A. Potapov, O.G. Litvinova, Mechanism of ferrite formation in a mixture of metallic powders, Poroshkovaya Metallurgiya 7 (163) (1976) 79–82.
[21] R.S. Devan, Y. Ma, B.K. Chougule, Mater. Chem. Phys. 115 (2009) 263–268.
[22] D.B. Shekhar, A.J. Pattayil, J. Am. Ceram. Soc. 91 (2008) 1976–1980.
[23] E.M.M. Ewais, M.M. Hessien, A.A. El-Geassy, J. Aust. Ceram. Soc. 44 (2008) 57–62.
[24] M. Sugimoto, J. Am. Ceram. Soc. 82 (1999) 269–280.
[25] Y.M.Z. Ahmed, M.M. Hessien, M.M. Rashad, I.A. Ibrahim, J. Magn. Magn. Mater. 321 (2009) 181–187.
[26] V. Sepelak, I. Bergmann, D. Menzel, A. Feldhoff, P. Heitjans, F.J. Litterst, K.D. Becker, J. Magn. Magn. Mater. 316 (2007) 764–767.