

Production of Pig Iron by Smelting of Blended Pre-Reduced Titaniferous Magnetite Ore and Hematite Ore Using Lean Grade Coal

Bitan Kumar Sarkar, Akashdeep Agarwal, Rajib Dey, Gopes Chandra Das

I. INTRODUCTION

THE gradual depletion of high grade iron ore & coking coal reserves and growing environmental concerns have encouraged researchers to find for alternative ironmaking processes. Furthermore, during mining huge amounts of iron ore fines and coal fines are generated. But these iron fines cannot be treated as charge material in a conventional blast furnace because fines will either impede the rate of the counter current gas-solid reaction severely or will be fluidised and thus affect the productivity of the blast furnace [1]. On the contrary, many attempts are also made to exploit the other low grade sources of iron oxide such as TMO. TMO, mainly located in igneous rocks, contains inverse spinel structures like ilmenite ($\text{FeO}\cdot\text{TiO}_2$), magnetite (Fe_3O_4) and hercynite (FeAl_2O_4). The average composition of TMO in India is found to be 48–50 wt% Fe (total), 20–25 wt% TiO_2 and 0.3–0.8 wt% V_2O_5 [2].

Several attempts are made to find alternative routes to utilise the iron ore fines along with the non-coking coal. In this context, for alternative ironmaking processes composite pellets containing iron oxide and carbonaceous materials such as coke and coal can be a viable route as raw feeding material [3]. Nowadays in the laboratory scale such investigations on composite pellets are being extensively carried out in collaboration with other research institutes and industrial partners [4], [5]. Hence, studies on such agglomerates have drawn the attention of researchers all over the world [6]–[11]. Ahmed et al. [12] have studied the reduction kinetic of three different self-reducing mixtures (carbon bearing agglomerates) under inert atmosphere at varying different temperatures. The samples are heated up to a pre-set temperature (750–1100 °C at 50 °C intervals) for 2 h for the completion of reduction. It has been delineated that the activated charcoal is the most reactive carbon-bearing material. On the contrary, many attempts are also made to exploit the other low grade sources of iron oxide such as TMO. Direct pre-reduction of TMO has been widely investigated for many decades. It decreases power consumption which is essential for reduction and smelting of charge and electrode consumption during furnace operation [13]. It is a two-step process with preliminary metallization, i.e., pre-reduction of ore in the reduction furnace followed by SEAF smelting, which is very popular technology for titanium bearing magnetite ore [14]. The effect of size of ore particles on direct carbothermal reduction of titaniferous magnetite has been studied by [15]. They have found that ore particles larger than 15 mm are not fully reduced and degree of reduction is

Abstract—The rapid depletion of high-grade iron ore (Fe_2O_3) has gained attention on the use of other sources of iron ore. Titaniferous magnetite ore (TMO) is a special type of magnetite ore having high titania content (23.23% TiO_2 present in this case). Due to high TiO_2 content and high density, TMO cannot be treated by the conventional smelting reduction. In this present work, the TMO has been collected from high-grade metamorphic terrain of the Precambrian Chotanagpur gneissic complex situated in the eastern part of India (Shaltora area, Bankura district, West Bengal) and the hematite ore has been collected from Visakhapatnam Steel Plant (VSP), Visakhapatnam. At VSP, iron ore is received from Bailadila mines, Chattisgarh of M/s. National Mineral Development Corporation. The preliminary characterization of TMO and hematite ore (HMO) has been investigated by WDXRF, XRD and FESEM analyses. Similarly, good quality of coal (mainly coking coal) is also getting depleted fast. The basic purpose of this work is to find how lean grade coal can be utilised along with TMO for smelting to produce pig iron. Lean grade coal has been characterised by using TG/DTA, proximate and ultimate analyses. The boiler grade coal has been found to contain 28.08% of fixed carbon and 28.31% of volatile matter. TMO fines (below 75 μm) and HMO fines (below 75 μm) have been separately agglomerated with lean grade coal fines (below 75 μm) in the form of briquettes using binders like bentonite and molasses. These green briquettes are dried first in oven at 423 K for 30 min and then reduced isothermally in tube furnace over the temperature range of 1323 K, 1373 K and 1423 K for 30 min & 60 min. After reduction, the reduced briquettes are characterized by XRD and FESEM analyses. The best reduced TMO and HMO samples are taken and blended in three different weight percentage ratios of 1:4, 1:8 and 1:12 of TMO:HMO. The chemical analysis of three blended samples is carried out and degree of metallisation of iron is found to contain 89.38%, 92.12% and 93.12%, respectively. These three blended samples are briquetted using binder like bentonite and lime. Thereafter these blended briquettes are separately smelted in raising hearth furnace at 1773 K for 30 min. The pig iron formed is characterized using XRD, microscopic analysis. It can be concluded that 90% yield of pig iron can be achieved when the blend ratio of TMO:HMO is 1:4.5. This means for 90% yield, the maximum TMO that could be used in the blend is about 18%.

Keywords—Briquetting reduction, lean grade coal, smelting reduction, TMO.

Bitan Kumar Sarkar is with the Department of Metallurgical and Material Engineering, Jadavpur University, Kolkata-700032, India (e-mail: bitankumarsarkar@gmail.com).

Akashdeep Agarwal, Rajib Dey and Gopes Chandra Das are with the Department of Metallurgical and Material Engineering, Jadavpur University, Kolkata-700032, India.

also limited by formation of ulvospinel. Roshchin et al. [16] have investigated the solid-state carbothermal reduction of titanomagnetite concentrates using reductant of milled graphite electrodes at temperature range 1273 K to 1773 K. It has been found that the metallic iron began to form at the temperature range 1353 K to 1383 K and the reduction of titanium oxides began above 1488 K. Bitan et al. [2] have studied the isothermal reduction kinetic of TMO-coal composite briquettes at temperature range 1273-1473 K over the reduction time period of 3-60 minutes. Tu Hu et al. have studied reduction behaviour of Panzhihua titanomagnetite concentrates with coal at 1173-1573 K [17].

The structural complexity and high density of TMO makes the iron oxide difficult to treat and exploit. It is evident that the Indian TMO comprises of >20 wt% of TiO₂ which makes it even more difficult for usage as raw material. In this present study, the basic objective is to see how this low grade Indian TMO can be utilised for making of pig iron. This is achieved by two steps, first, briquettes of HMO fines-coal and TMO fines-coal are separately isothermally reduced. Then in the second step the best pre-reduced samples in each case are then blended in different weight percentage ratio and subjected to smelting to get the pig iron.

II. MATERIALS AND METHODS

A. Characterization of Ore

The HMO for the above experiment has been collected from VSP, Visakhapatnam. The TMO has been collected from Shaltora area (23°33'N, 86°56'E), Bankura district, West Bengal, India. After consecutive crushing and grinding, the fine ores of TMO and HMO have been passed through BSS Standard -200 mesh sieve separately by using mechanical shaker and particle size below 75 μm is taken for further experimental work. The composition of HMO & TMO have been analysed by x-ray fluorescence (XRF; PAN analytical) and are given in Tables I and II, respectively. It is observed that TMO contains comparatively very high TiO₂ content (23.23%) along with V₂O₅ (0.408%). The phase analyses have been performed by x-ray diffractometers (XRD; Rigaku Ultima III) and are depicted in Figs. 1 and 2, respectively. Ilmenite (FeTiO₃), magnetite (Fe₃O₄) and hercynite (FeAl₂O₄) are observed as the major phases present in TMO. On the contrary, HMO mainly comprises of phases like hematite (Fe₂O₃), silica (SiO₂) and alumina (Al₂O₃).

TABLE I
XRF ANALYSIS OF TMO

Element/Compound	Fe(T)	TiO ₂	SiO ₂	Al ₂ O ₃	MnO	MgO	CaO	Na ₂ O	P ₂ O ₅	V ₂ O ₅	K ₂ O	Ni	Co
Concentration	48.96	23.23	1.95	3.8	0.24	2.09	0.16	0.15	0.02	0.408	0.04	287(ppm)	193(ppm)

TABLE II
XRF ANALYSIS OF HMO

Element/Compound	Fe(T)	TiO ₂	SiO ₂	Al ₂ O ₃	MnO	MgO	CaO	Na ₂ O	P ₂ O ₅	S	K ₂ O
Concentration	64.39	0.18	4.02	2.26	0.06	0.25	0.39	0.02	0.09	0.1	<0.01

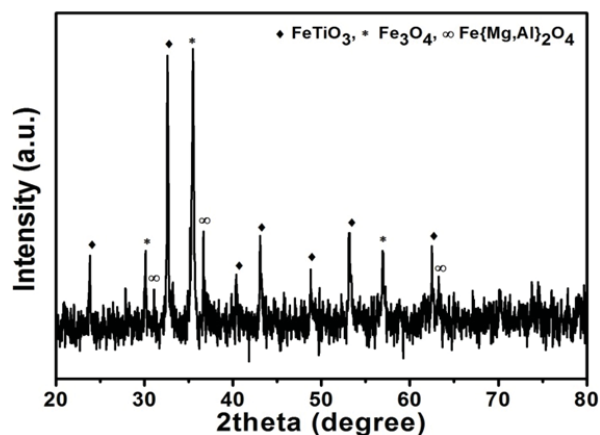


Fig. 1 XRD analysis of TMO

B. Characterization of Boiler Grade Coal

Lean grade coal, used as reductant for carbothermal reduction, has been crushed and ground to get fine particles below 75 μm size. Preliminarily, the composition of coal is analysed by standard proximate analysis and is presented in Table III. Thermo gravimetric-differential thermal analysis (TG/DTA; Perkin Elmer) of coal is also performed under nitrogen atmosphere from room temperature to 1273 K and is

shown in Fig. 3. It is observed that at around 373-383 K (100-110 °C) and 673-873 K (400-600 °C), 7-8 wt% of moisture content and more than 25 wt% of volatile matter content of coal are removed, respectively.

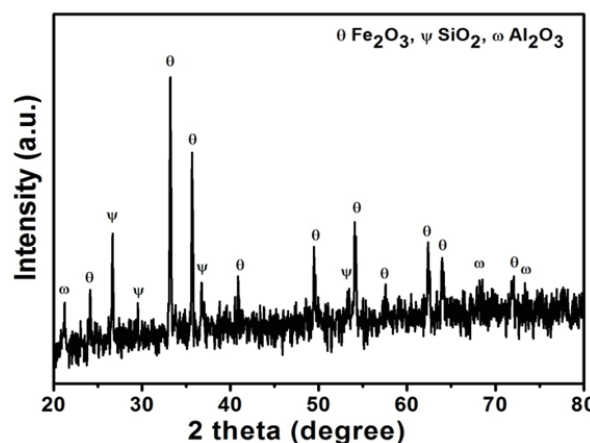


Fig. 2 XRD analysis of HMO

TABLE III
PROXIMATE ANALYSIS OF BOILER GRADE COAL

Boiler Grade Coal	Fixed carbon (%)	Volatile matter (%)	Moisture (%)	Ash (%)
Composition	28.08	28.31	7.4	36.21

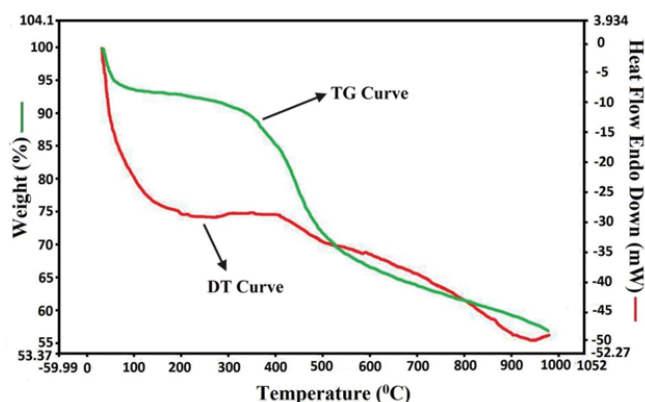


Fig. 3 TG/DT analysis of Lean Grade Coal

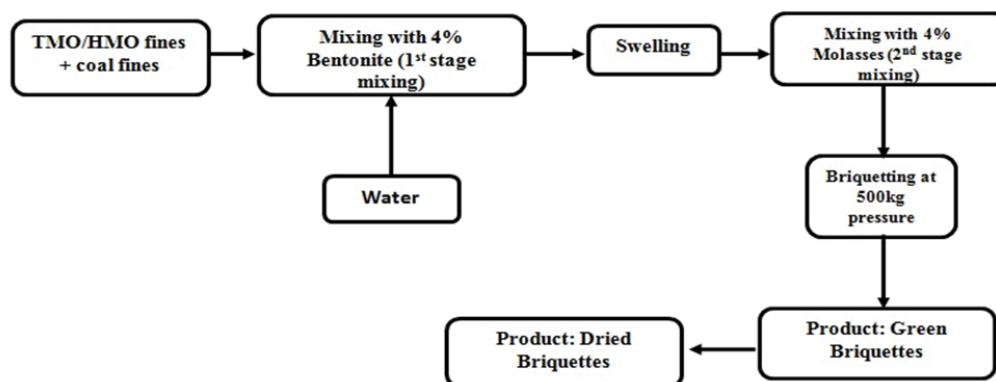


Fig. 4 Flowchart for making briquettes

C. Briquetting

TMO and HMO fines (>75 μm particle size) are taken separately and then mixed homogeneously with stoichiometric weight percentage of lean grade coal fines and binders (bentonite, molasses and moisture). It is then pressed at a pressure of 49.03 MPa by using dyes to form cylindrical briquettes. The green briquettes are approximately 10 grams in weight with 25 mm of diameter and 12 mm of height. These briquettes are dried and subjected to perform series of reduction experiments. The flow chart for the formation of briquettes is shown in Fig. 4.

D. Experimental Procedure

Briquettes of TMO-coal and HMO-coal are separately reduced at isothermal condition in a standard tube furnace varying temperature from 1323 to 1423 K and reduction time of 30 minutes and 60 minutes. The maximum reduced briquettes for both TMO-coal & HMO-coal are taken and are then blended in different weight percentage ratios as in 1:4, 1:8 and 1:12. Thereafter, the blended samples are then again briquetted with adding lime & moisture and subsequently smelted using graphite crucible at 1773K for 30 minutes in raising hearth furnace. The chemical analysis after blending and microstructure analysis of pig iron after smelting are performed.

III. RESULTS AND DISCUSSIONS

A. Effect of Reductant, Temperature and Time on Reduction

Proximate analysis of coal has revealed that coal contains 28.08% of fixed carbon and 28.31% of volatile matter. The amount of volatile matter present is significantly large enough to play a crucial role in the carbothermal reduction experiments. From TG/DTA (Fig. 3), it is observed that the

volatile matter starts to release above 673 K. The reduction of briquettes has been carried out at 1323, 1373 & 1423 K for a period of 30 minutes and 60 minutes. Sah et al. [18] have reported that coal devolatilisation and reduction of iron oxide occur simultaneously. Reduction of iron oxide is actively governed by H₂ and CO gases which produce due to coal devolatilisation and char gasification. It is also reported that upto 1083K, H₂ gas acts as a better reductant than that of CO gas [19]. Gui-su Liu et al. [20] have shown that devolatilisation of coal produces solid coke, tar and gases like H₂ and CO.

For reduction of briquettes of TMO-coal and HMO-coal, a major difficulty with experiments is that the extent of the reduction cannot be found out directly from the weight loss of the briquettes, since the weight loss of the briquettes arises not only from oxygen and carbon loss, but also the loss of binders, volatile matter and residual moisture present in pellet. Hence only weight loss of the briquettes is not sufficient; some additional measurements are done to estimate the weight percentage loss (α) which is defined as [2]:

$$\text{Weight Loss, } \alpha = \frac{W_t}{W_0} * 100$$

where, W_t is the weight loss due to oxygen from TMO/HMO as well as of fixed carbon of coal during isothermal reduction of briquette for t minutes and W_0 stands for the total content of reducible oxygen in TMO/HMO as well as of total fixed carbon content of coal. So, α gives the isothermal weight percentage loss as a function of time and is shown in Figs. 5 (a) and (b).

From Fig. 5 (a), it is observed that with increase in reduction temperature from 1323 K to 1423 K α for TMO is also increased from 65.44% to 77.34%, respectively, for reduction time of 30 minutes. As the reduction of TMO

requires high temperature, the α for TMO is greatly enhanced with raising temperature from 1373 K to 1423 K. Again with increase in the duration of reduction time from 30 minutes to 60 minutes, the α for TMO at 1423K has been observed to maximum value of 83.14%. On the other hand, Fig. 5 (b) shows the variation of α for HMO with temperature at different reduction time. At reduction time of 30 minutes, with increasing temperature from 1323K to 1423K, α for HMO is also increases from 79.14% to 82.75%, respectively. Maximum value of α for HMO is observed as 84.01% at temperature 1423K for reduction time of 60 minutes.

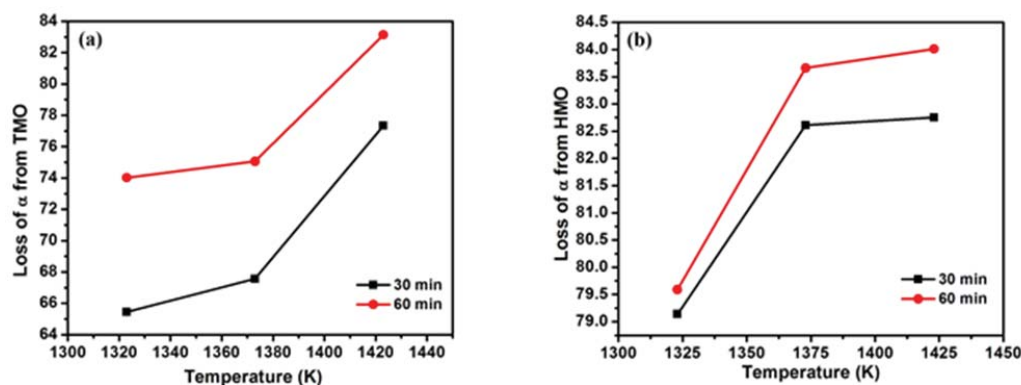


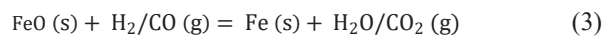
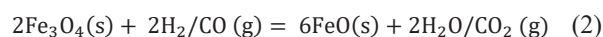
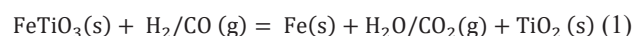
Fig. 5 Fractional loss α Vs temperature (K) for reduced briquettes of (a) TMO and (b) HMO at 30 and 60 minutes

B. Phase Characterization after Reduction

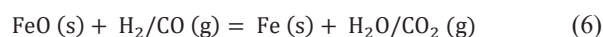
Phase characterisation of all reduced briquettes of TMO-coal and HMO-coal are carried out separately by using XRD analysis and is tabulated in Table IV. In case of composite mixtures, the overall reduction process is mainly driven by the indirect reaction of gas-solid interactions rather than the direct contact between solid iron and carbon particles which is indeed very limited [21]. It can be observed that the rate of reduction is greatly enhanced by increasing temperature. In case of TMO-coal briquettes, the reduction rate at 1323K is low and so the ilmenite and magnetite phases are present along with the presence of iron peaks (Table IV) after the reduction for a period of 30 minutes. Gupta et al. have reported that above 1113 K, magnetite (Fe_3O_4) is initially reduced to wustite (FeO) and then wustite to iron (Fe) reduction by solid carbon and CO & H_2 gases, respectively [22]. The reason behind the peak of TiO_2 can be explained as that during the reduction the ilmenite phase breaks to form FeO & TiO_2 . At 1373K, some fraction of FeO recombines with TiO_2 to form ilmenite while the other FeO further reduces to produce iron. The reduction rate increases remarkably with increasing temperature. At temperature 1423 K for 60 minutes of reduction time, only a strong intensity peak of iron is observed along with a small peak of SiO_2 which comes from the ash content of coal and the corresponding XRD has been shown in Fig. 6. On the other hand, the observed phases of the reduced HMO-coal briquettes at varying temperatures and times are shown in Table IV. Reduction of haematite (Fe_2O_3) to iron (Fe) by gaseous reductants such as CO and H_2 is known to be multistep

process having intermediate products of magnetite and wustite. At temperature 1323 K for of reduction time of 30 minutes a significant intensities of iron peaks are observed along with small intensity peaks of magnetite, wustite, silica and alumina. As the reduction temperature increases to 1423 K, the only predominant peaks of iron are present along with small peak corresponding to SiO_2 which comes from the ash content of coal. The probable chemical reactions that occurred are shown as (1)-(6):

In case of TMO,



In case of HMO,



Field emission scanning electron microscopic analysis (FESEM; Hitachi S-4800) is performed to observe the surface morphology of the reduced briquettes. The FESEM images of maximum reduced briquettes at temperature 1423K for reduction time of 60 minutes in both the case for TMO-coal and HMO-coal have been shown in Figs. 8 (a) and (b),

respectively. It is observed that the surface of the reduced samples is decorated with the spherical shaped iron particles. The aggregates of iron particles have grown into large spherical shape and are apparently isolated from the oxide matrix both for TMO-coal & HMO-coal reduced briquettes.

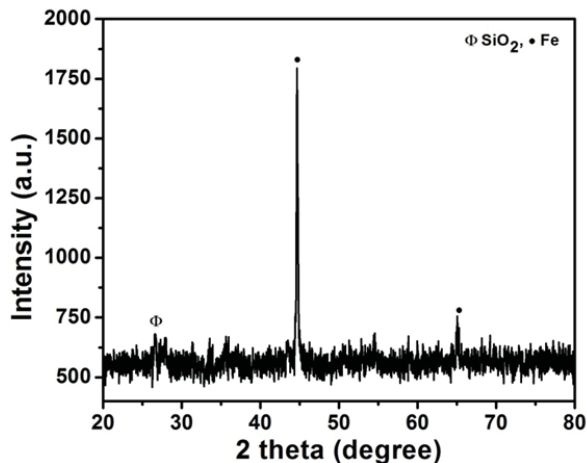


Fig. 6 XRD of reduced TMO at 1423K for 60 min

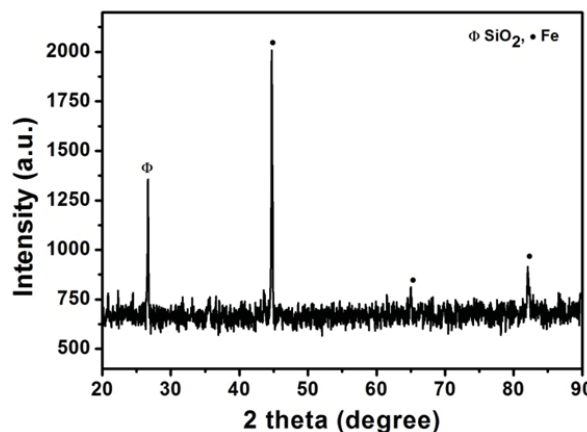


Fig. 7 XRD of reduced HMO at 1423K for 60 min

TABLE IV
 PHASES OBSERVED IN REDUCED BRIQUETTES OF TMO-COAL AND HMO-COAL AT DIFFERENT TEMPERATURES AND TIMES

Temperature (K)	Reduction time (min)	Identified phases	
		For TMO	For HMO
1323	30	Fe, FeTiO ₃ , Fe ₃ O ₄ , TiO ₂	Fe, Fe ₃ O ₄ , FeO, SiO ₂ , Al ₂ O ₃
1323	60	Fe, SiO ₂ , TiO ₂	Fe, FeO, SiO ₂ , Al ₂ O ₃
1373	30	Fe, FeTiO ₃ , TiO ₂	Fe, Fe ₃ O ₄ , FeO, SiO ₂ , Al ₂ O ₃
1373	60	Fe, SiO ₂ , TiO ₂	Fe, SiO ₂ , Al ₂ O ₃
1423	30	Fe, SiO ₂	Fe, SiO ₂
1423	60	Fe, SiO ₂	Fe, SiO ₂

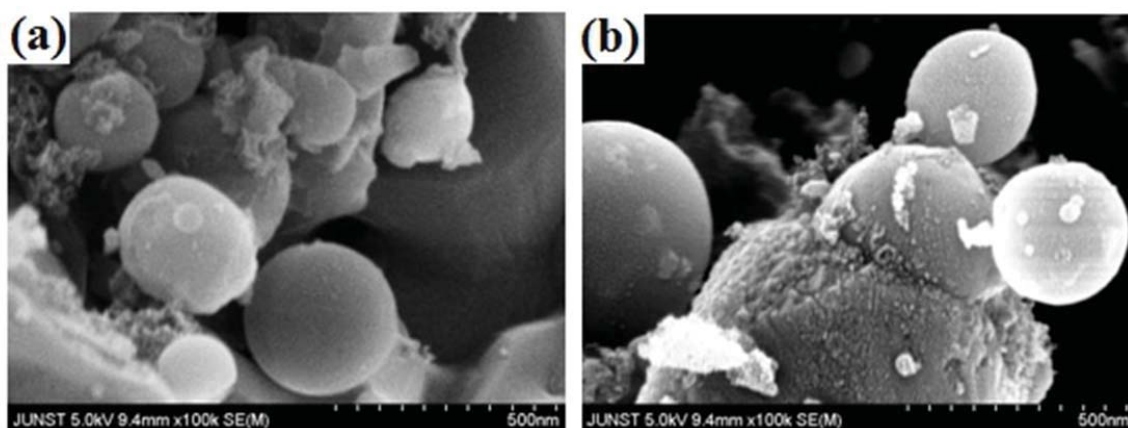


Fig. 8 FESEM images of reduced briquettes of (a) TMO and (b) HMO after 60 minute at 1423K

C. Blending in Different Ratio and Its Chemical Analysis

The degree of metallisation of the maximum reduced TMO-coal briquette and HMO-coal briquette have also been evaluated separately by titrimetric method and are found to be 88.18% and 93.20%, respectively. The maximum reduced TMO-coal briquette and HMO-coal briquette are blended in three different ratios such as 1:4, 1:8 and 1:12. The purpose of

blending is to minimise %TiO₂ in the charge-mix before smelting as TMO contains 23.23% of TiO₂. Moreover, maximum of only 8-10% TiO₂ (in South Africa and some parts of China) can be used for smelting in the conventional blast furnace because the presence of high TiO₂ content influences the material swelling during reduction as well as the development of titanium carbides and nitrides in the blast

furnace slag leads to a high viscous slag with entrained iron creating abnormal performance of the blast furnace. Here pre-reduction followed by smelting is performed because solid state direct reduction before smelting operation helps to reduce the consumption of coking coal. In this study, pre-reduction is carried out using boiler grade coal as a reductant and in addition to that low grade iron ore (TMO) is also used along with high grade iron ore (HMO).

The degree of metallisation of three blended samples has been evaluated by standard titrimetric method (IS 15774: 2007) and is tabulated in Table V. Therefore, the degree of metallisation may be represented by:

$$\text{Degree of Metallisation} = \frac{\text{Fe}_{\text{Metallic}}}{\text{Fe}_{\text{Total}}} * 100 \%$$

where, $\text{Fe}_{\text{Metallic}}$ is the weight of metallic Fe in the blended sample, which is measured by chemical titration analysis and Fe_{Total} is the total Fe content in blended sample. On the basis of degree of metallisation of the blended samples a graph has been plotted to degree of Metallization (%) against percentage of TMO in the blended mixture and shown in Fig. 9. From this graph, it can be inferred that the maximum of 18% TMO can be blended with HMO after pre-reduction to get minimum 90% of degree of metallisation. In this context, 90% yield of pig iron can be achieved by taking the blend ratio of TMO:HMO is 1:4.5.

TABLE V
 DEGREE OF METALLISATION (%) OBTAINED FROM THREE BLENDED SAMPLES

Sample (TMO:HMO)	Degree of Metallisation (%)
1:4	89.38
1:8	92.12
1:12	93.12

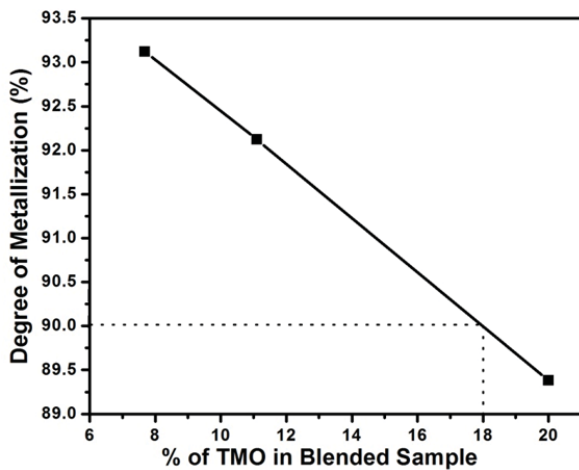


Fig. 9 Plot of degree of Metallization (%) Vs percentage of TMO in the blended mixture

D. Smelting of Blended Samples

The three blended samples are separately mixed homogeneously with 1% lime and few drops of water and pressed by using dyes to form three briquettes. These briquettes are then smelted at 1723 K for 30 min of time span

in raising hearth furnace. The pig iron, that has been obtained, are characterised by XRD analysis (Figs. 10-12). It is observed that as the ratio changes from 1:4 to 1:12, intensity of iron peak increases which indicate formation of more of pig iron after smelting which is expected.

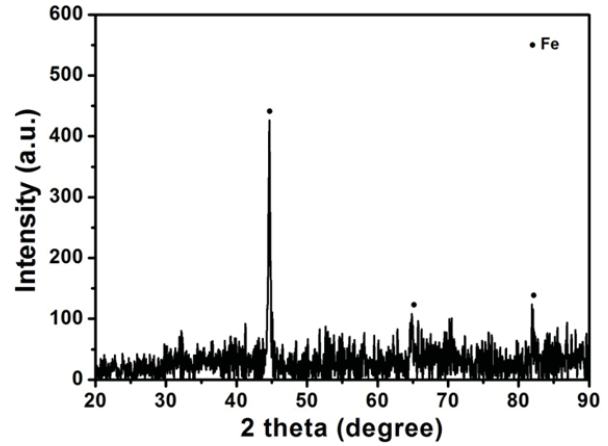


Fig. 10 XRD of the metal formed on smelting of blended mixture 1:4

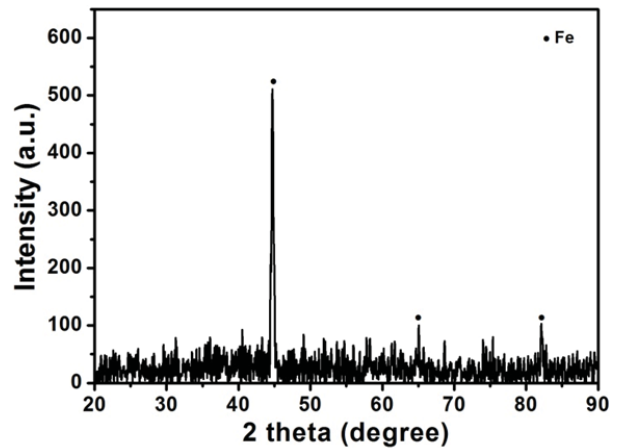


Fig. 11 XRD of the metal formed on smelting of blended mixture 1:8

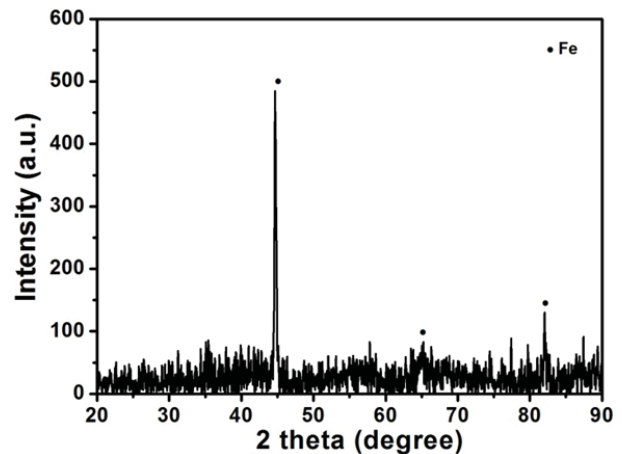


Fig. 12 XRD of the metal formed on smelting of blended mixture 1:12

E. Optical Microstructure Analysis of the Pig Iron

The surface morphology is studied by optical microstructure analysis (Fig. 13). The scattered black colour region seems to be gradually localised from blending ratio of 1:4 to 1:12. This observation can be explained by the following reason. The presence of high TiO₂ content in case of

blended sample of 1:4 ratio (Fig. 13 (a)) leads to the non-uniform and poor slag-metal separation after smelting. So entrapment of slag is depicted by the black colour region. As the blending ratio increases to 1:8 to 1:12, the slag separation is more and the corresponding black region decreases (Figs. 13 (b) and (c)).

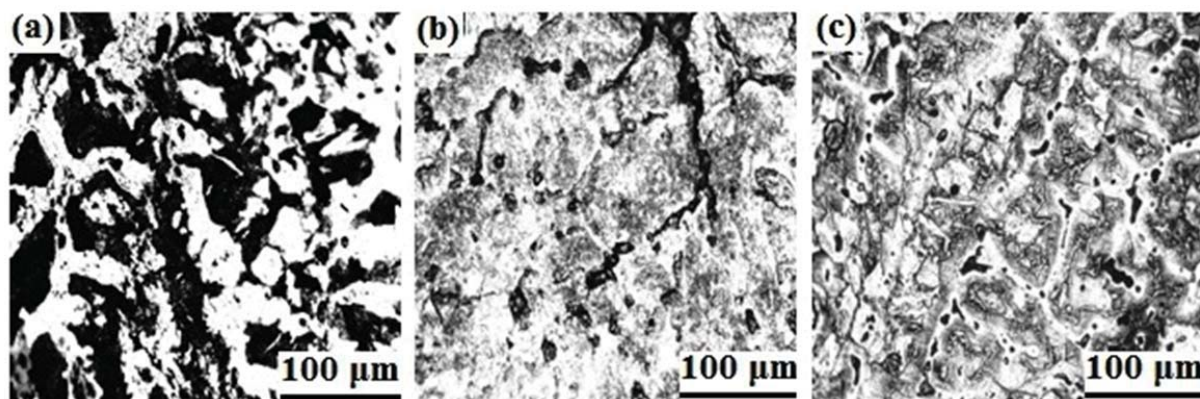


Fig. 13 Microstructures of metal formed on smelting of (a) 1:4 Blending mixture, (b) 1:8 Blending Mixture, (c) 1:12 Blending Mixture

IV. CONCLUSION

TMO has been used as an alternative source of iron ore. Briquettes of TMO-coal and HMO-coal have been used for pre-reduction with varying temperature 1323, 1373 & 1423 K and reduction time of 30 & 60 minutes. The maximum reduction is observed at 1423 K for 60 minutes of reduction time for both the cases. Hence, this reduced samples are taken for blending with three different wt% ratio of TMO:HMO as 1:4, 1:8 & 1:12 and then it is briquetted with adding lime (1%) followed by smelting at 1773 K for 30 minutes. From the chemical analysis it can be concluded that 90% of metallisation can be achieved with minimum blending ratio 1:4.5 of TMO:HMO. In other words, the maximum of 18% TMO can be blended with HMO after pre-reduction to get minimum 90% of metallic iron.

ACKNOWLEDGMENT

The authors would like to thank Mr. Anirban Sur, Sr. Chemist, Geological Survey of India (Eastern Region), Kolkata, (India). We would also like to acknowledge Dr. Saikat Samanta, R & D, Essar Steel India Pvt. Ltd. for his valuable suggestions and assistance. One of the authors (Bitan Kumar Sarkar) acknowledges the financial support under the scheme "UGC-BSR Research Fellowship in Science for Meritorious Students, 2012-13 (7-88/2007 (BSR))".

REFERENCE

- [1] G. M. Chowdhury, G. G. Roy and S. K. Roy: 'Reduction kinetics of iron ore-graphite composite pellets in a packed-bed reactor under inert and reactive atmospheres', *Metall. Mater. Trans. B*, 2008, 39, 160-178.
- [2] Bitan Kumar Sarkar, Saikat Samanta, Rajib Dey and Gopes Chandra Das, A Study on Reduction Kinetics of Titaniferous Magnetite Ore Using Lean Grade Coal, *International Journal of Mineral Processing*, 152, 36-45 (2016).

- [3] H. M. Ahmed, N. Viswanathan and B. Bjorkman: 'Composite pellets – a potential raw material for Iron-making', *Steel Res. Int.*, 2014, 85, 293-306.
- [4] R. Robinson: 'Studies in low temperature self-reduction of by-products from integrated iron and steelmaking', Luleå tekniska universitet, Luleå tekniska universitet, Doctoral thesis (2008), 69.
- [5] D. Adolfsson, R. Robinson, J. Blagojevic and F. Su: 'Assessment of ladle slag as binder alternative for cold bonded briquettes,' *Global Symposium on Recycling, Waste Treatment and Clean Technology*, Cancun, Mexico, October 12-15, 2008, Minerals, Metals & Materials Society.
- [6] S. Ueda, K. Watanabe, K. Yanagiya, R. Inoue and T. Ariyama: 'Improvement of reactivity of carbon iron ore composite with biomass char for blast furnace', *ISIJ Int.*, 2009, 49, 1505-1512.
- [7] S. Ueda, K. Yanagiya, K. Watanabe, T. Murakami, R. Inoue and T. Ariyama: 'Reaction model and reduction behavior of carbon iron ore composite in blast furnace', *ISIJ Int.*, 2009, 49, 827-836.
- [8] T. Murakami, T. Nishimura and E. Kasai: 'Lowering reduction temperature of iron ore and carbon composite by using ores with high combined water content', *ISIJ Int.*, 2009, 49, 1686-1693.
- [9] Y. Matsui, M. Sawayama, A. Kasai, Y. Yamagata and F. Noma: 'Reduction behavior of carbon composite iron ore hot briquette in shaft furnace and scope on blast furnace performance reinforcement', *ISIJ Int.*, 2003, 43, 1904-1912.
- [10] S. K. Dutta, A. Ghosh: 'Study of nonisothermal reduction of iron ore-coal/char composite pellet', *MMTB*, 1994, 25, 15-26.
- [11] S. K. Dutta, A. Ghosh: 'A new method for measurement of degree of reduction in composite pellets of iron ore with carbonaceous matter', *ISIJ Int.*, 1993, 33, 1104-1106.
- [12] H. M. Ahmed, N. N. Viswanathan and B. Björkman, Isothermal reduction kinetics of self-reducing mixtures, *Ironmaking & Steelmaking*, DOI 10.1080/03019233.2016.1165497 (2016).
- [13] R. H. Nafziger and R. R. Gordan, Pre-reduction and melting of domestic titaniferous materials, *Metallurgical Transactions B*, 1983, pp-55-62.
- [14] V. E. Roshchin, A. V. Asanov and A. V. Roshchin, Possibilities of two-stage processing of titaniferous magnetite ore concentrates, *Russian Metallurgy (Metally)*, 2011, pp-499-508.
- [15] M. M. Manamela and P. C. Pistorius, Ore size does affect direct reduction of titaniferous magnetite, *The Journal of the South African institute of Mining and Metallurgy*, 2005, pp-183-186.
- [16] V. E. Roshchin, A. V. Asanov and A. V. Roshchin, Solid-phase pre-reduction of iron-vanadium concentrates and liquid-phase separation of the products of their reduction, *Russian Metallurgy (Metally)*, 2010, pp-1001-08.

- [17] Tu Hu, Xuewei Lv, Chenguang Bai, Zhingang Lun and Guibao Qiu, Reduction behaviour of panzhihua titanomagnetite concentrates with coal, *Metallurgical and Materials Transactions B*, 2013, pp-252-260.
- [18] R. Sah, S. K. Dutta, Kinetic studies of iron ore-coal composite pellet reduction by TG/DTA, *Trans Indian Inst Met*, 64 (6) (2011), 583-591.
- [19] H. W. Gudenau, D. Senk, S. Wang, K. De Melo Martins, C. Stephany, Research in the reduction of iron ore agglomerates including coal and c-containing dust, *ISIJ Internationals*, 45 (2005), 603-608.
- [20] G. Liu, V. Strezov, J. A. Lucas, L. J. Wibberley, Thermal investigations of direct iron ore reduction with coal, *Thermochimica acta*, 410 (2004), 133-140.
- [21] W. Lu and D. F. Huang: 'The evolution of ironmaking process based on coal-containing iron ore agglomerates', *ISIJ Int.*, 2001, 41, 807– 812.
- [22] A. K. Vaish, R. C. Gupta, S. P. Mehrotra, Thermodynamic and kinetic aspects of the smelting reduction of multimetallic Indian magnetite ore, *Journal of Metallurgy and Materials Science*, 48 (2006), 1-12.