Mogylatenko V.G.[1], Shapovalov V.O.[2], Biktagirov F.K.[2], Kozin R.V.[2]
([1]Igor Sikorsky Kyiv Polytechnic Institute; [2]E.O. Paton Electric Welding Institute of the NAS of Ukraine, Kyiv)

THERMAL DECOMPOSITION OF HEMATITE PELLETS DURING PLASMA–ARC SMELTING IN ARGON ATMOSPHERE

E–mail: vmogilatenko@gmail.com

In 2020, fossil energy sources in the EU accounted for 37%, and renewable energy sources – 38%.The main sources of greenhouse gas emissions in metallurgy are blast furnaces, open hearth furnaces, gas heating furnaces and converters. Greenhouse gases are formed at almost all stages of metallurgical redistribution: during fuel combustion, during metal decarburization reactions, during deoxidation of the melt with carbon, during decomposition of flux components, etc.

Sometimes researchers follow the path of improving or optimizing existing technologies and options for processing cast iron or recovering iron [1–3]. It was shown, for example, that the simultaneous use of oxygen converters and arc furnaces for the processing of cast iron can reduce the total emission of carbon dioxide by up to 20%.
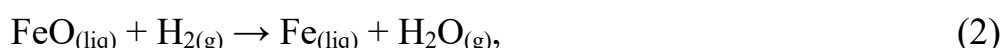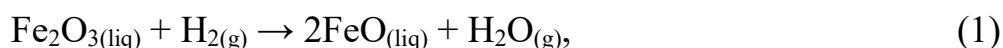
Reduction of iron ore with pure hydrogen in a direct reduction mine furnace depends on many factors, in particular, on temperature, type of iron ore (magnetite, hematite, goethite), ratio of H_2/CO in the mixture of gases, porosity of the mineral (ore), gas consumption, concentration of the diluent of the gaseous atmosphere (He, Ar, N_2), etc. [4–8].

Solid–phase reduction of iron oxides is recommended to be carried out either in countercurrent mine furnaces or in fluidized bed furnaces [9, 10].

As can be seen from the diagram Fe – O, there is a possibility of realizing the iron recovery process from the oxide melt at a temperature above 1870 K. The analysis of literature data shows that most of the research is aimed mainly at the recovery of iron ore in the solid state, and there is not enough research in the field of hydrogen recovery of liquid iron ore.

During plasma welding, the temperature of the arc is more than 4000 °C and dissociation of hydrogen molecules, their ionization and excitation take place in the arc zone [11–13]. It was established that the rate of recovery of iron above the melting temperature of wustite becomes 13.2 times greater than in the solid phase.

It should be noted that magnetite is a mixture of hematite and wustite. Then the reaction of hematite reduction using hydrogen takes place in two stages:

$$Fe_2O_{3(liq)} + H_{2(g)} \rightarrow 2FeO_{(liq)} + H_2O_{(g)}, \tag{1}$$
$$FeO_{(liq)} + H_{2(g)} \rightarrow Fe_{(liq)} + H_2O_{(g)}, \tag{2}$$

which agrees with the opinion of the authors of the works [12, 13].

Currently, attention is being paid to the efficiency of hydrogen use in recovery processes and there are studies [13–15] in which, in addition to research on iron recovery, optimization of technological processes is carried out to reduce the consumption of hydrogen, taking into account the rather high cost of its production, storage and transportation.

Recovery of iron during plasma melting is ensured by the intensification of recovery processes both due to the use of active hydrogen (H^+, H_2^+, H_3^+, H), and high plasma temperature. What is the effect of high temperature, apart from the creation of plasma, and inert gas, which is used as a diluent for hydrogen and forms a gaseous reducing atmosphere together with hydrogen? The answer to this question is provided by classical thermodynamics. In the table 1 and in fig. 1 shows the data for calculating the equilibrium temperatures of decomposition reactions of iron oxides.

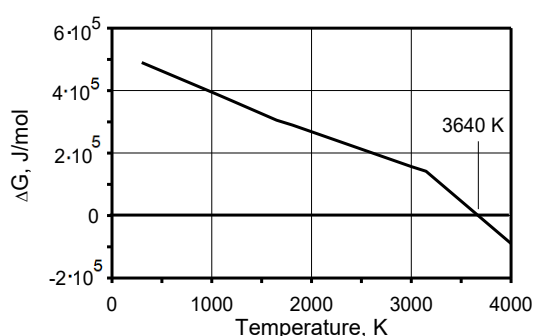Table 1 – Equilibrium temperatures of iron oxide decomposition reactions

Reaction	Reaction equilibrium temperature ($\Delta G = 0$), K	Reaction	Reaction equilibrium temperature ($\Delta G = 0$), K
$6Fe_2O_3 = 4Fe_3O_4 + O_2$	1580	$2Fe_3O_4 = 6FeO + O_2$	3148
$2Fe_2O_3 = 4FeO + O_2$	2250	$1/2Fe_3O_4 = 3/2Fe + O_2$	3515
$2/3Fe_2O_3 = 4/3Fe + O_2$	3154	$2FeO = 2Fe + O_2$	3640
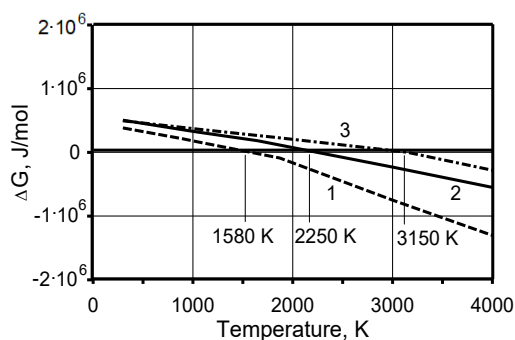
a
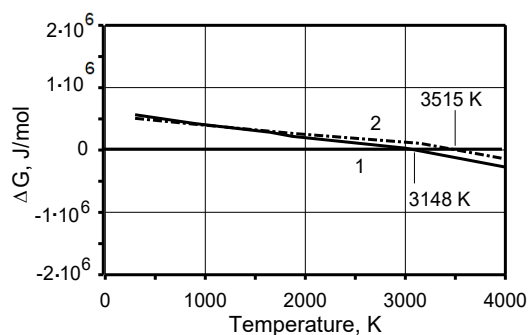
b

c

Fig. 1. Gibbs free energy change of iron oxide decomposition reactions:

a – hematite (1 – $6Fe_2O_3 = 4Fe_3O_4 + O_2$,

2 – $2Fe_2O_3 = 4FeO + O_2$,

3 – $2/3Fe_2O_3 = 4/3Fe + O_2$);

b – magnetite (1 – $2Fe_3O_4 = 6FeO + O_2$,

2 – $1/2Fe_3O_4 = 3/2Fe + O_2$);

c – wustite ($2FeO = 2Fe + O_2$)

From the given data it follows: firstly, that reaching temperatures above 3000 K is possible only with the use of highly concentrated heating sources (for example, plasma), and secondly, that there is no reason to use hydrogen for the reduction of iron from the very beginning of melting, if at the plasma temperature all the given reactions go to the end. As can be seen from the table 2, only small kinetic restrictions can be imposed on the course of reactions, which will lead to the slow progress of some of them at temperatures above 4000 K.

As can be seen from the table 2, any type of iron ore can be thermally decomposed: hematite, magnetite, goethite (hydroxide FeO(OH) composition: Fe_2O_3 – 89.9% and H_2O – 10.1%). However, the reactions of hematite or goethite decomposition after its dehydration have the greatest thermodynamic probability of passage. Reduction reactions can take place simultaneously. As a result, an iron melt will be obtained and

reduction of hematite using hydrogen can be considered a one– and not a two–stage process.

Table 2 – Gibbs free energy change and equilibrium constant of iron oxide decomposition reactions at 4000 K

Reaction	$lgK_p^{4000\,K}$	$\Delta G^{4000\,K}$, J	Reaction	$lgK_p^{4000\,K}$	$\Delta G^{4000\,K}$, J
$6Fe_2O_3 = 4Fe_3O_4 + O_2$	17.0610	−1303463	$2Fe_3O_4 = 6FeO + O_2$	3.5956	−274702
$2Fe_2O_3 = 4FeO + O_2$	7.1900	−549314	$1/2Fe_3O_4 = 3/2Fe + O_2$	1.8681	−142725
$2/3Fe_2O_3 = 4/3Fe + O_2$	3.6132	−276049	$FeO = Fe + O_2$	1.1761	−89853

In order to check the possibility of decomposition of iron oxides, samples of pellets were melted using argon as a plasma–forming gas. In fig. 2 shows the result of X–ray tested of the original pellet. The composition of the pellet is a mixture of 95.0% hematite and 5.0% quartz sand as an accompanying substance.
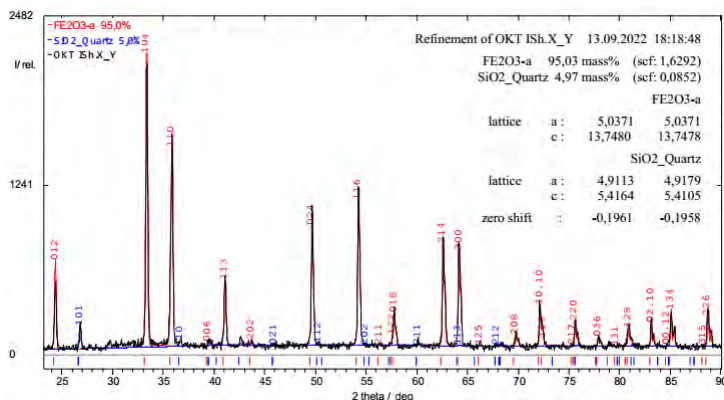

Fig. 2. Result of X–ray tested the original unfluxed pellet sample

After plasma–arc melting in an argon atmosphere for 60 seconds, the amount of hematite in the solidified sample decreased to 8.9%. But magnetite (59.8%), wustite (23.2%) and iron and/or calcium silicate $(Fe,Ca)_2SiO_4$ appear in the amount of 8.1% (Fig. 3). Rather, $2FeO·SiO_4$ is formed, since calcium was not detected in the initial sample of the unfluxed pellet.
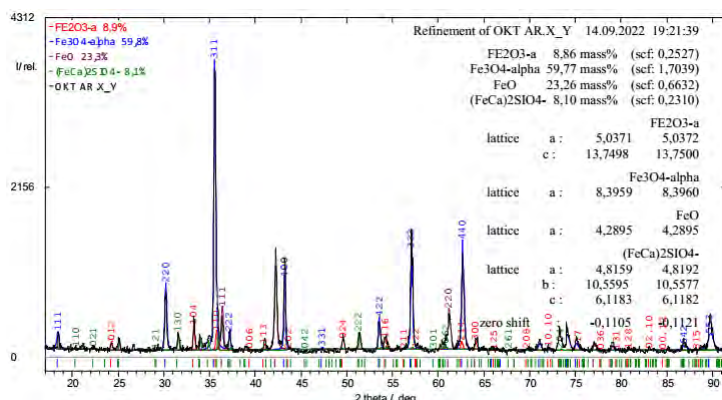
Fig. 3. Result of X–ray tested the solidified unfluxed pellet sample after plasma–arc melting of the pellet for 60 s in an argon atmosphere

The recalculation of the composition of the samples for the oxygen content showed that its amount in the original pellet is 31.2%, and after plasma–arc melting the oxygen content in the sample decreased by 4.3% to 26.9%, i.e. by 13.8% from the original oxygen content.

So:

1 – the reaction of thermal decomposition of hematite to iron in a liquid state begins at a temperature of 3150 K;

2 – judging by the extrapolation of dependencies 1 and 3 in Fig. 1a at temperatures above 5000 K, the hematite decomposition reaction to iron and not to magnetite will prevail;

3 – melting of hematite by plasma-arc melting in argon atmosphere allows to reduce oxygen content in melt by about 15%;

4 – the thermal decomposition of hematite by hydrogen deoxidation should not be underestimated, since it is one of the steps for producing green iron and saves hydrogen.

Literature:

1. Лисиенко В. Г. Сравнительная эмиссия парникового газа CO_2 в переделах черной металлургии / В. Г. Лисиенко, А. В. Лаптева, Ю. Н. Чесноков, В. В. Луговкин // Известия ВУЗов. Черная металлургия. – 2015. – № 9. – С. 625 – 629.

2. Лисиенко В. Г. Эмиссия парниковых газов при различных процессах черной металлургии / В. Г. Лисиенко, А. В. Лаптева // Культура и экология –

основы устойчивого развития россии. От «зеленого» университета к зеленой экономике. Ч. 1.—Екатеринбург, 2016. – С. 76 – 79.

3. 4. Lisienko V. G. Application of the Triad of Blast Furnace, Oxygen Converterand Electric ARC Furnace for Reducing of Carbon Footprint / V. G. Lisienko, Yu. N. Chesnokov, A. V. Lapteva // Steel in Translation. – 2017 – Vol. 47. – № 8. – P. 523 – 527. Режим доступу: https://www.researchgate.net/publication/321272355

4. Zuo Hb. Reduction kinetics of iron oxide pellets with H_2 and CO mixtures / Hb. Zuo, C. Wang, Jj. Dong., Kx. Jiao, Rs. Xu // International Journal of Minerals, Metallurgy and Materials. – 2015. – V. 22. – № 7. – P. 688–696. DOI: 10.1007/s12613–015–1123–x. Режим доступу:https://www.researchgate.net/publication/282499310

5. Donghui Liu. Study on the controlling steps and reduction kinetics of iron oxide briquettes with CO–H2 mixtures / Donghui Liu, Xiaozhe Wang, Jianliang Zhang, Zhengjian Liu, Kexin Jiao, Xingle Liu, Rongrong Wang // Metall. Res. Technol. – 2017. – V. 114. – № 6. 611. DOI: 10.1051/metal/2017072.

Режим доступу: https://www.researchgate.net/publication/320229625

6. Hala H. Abd El–Gawad. Recycle of El–Dekhaila iron oxide waste and reducing it by hydrogen / Hala H. Abd El–Gawad, Mohamed Rafi, M. E. H. Shalabi. Режим доступу: https://www.researchgate.net/publication/306099434

7. Ranzani da Costa A. Modelling a new, low CO2 emissions,hydrogen steelmaking process / A. Ranzani da Costa, D. Wagner, F. Patisson // Journal of Cleaner Production.–2013.–V.13.–№46.27–35. Режим доступу: https://arxiv.org/abs/1402.1715

8. Kazemi M.. Experimental and Modeling Study on Reduction of Hematite Pellets by Hydrogen Gas / M. Kazemi, M. S. Pour, D. Sichen // Metallurgical and Materials Transactions B, 2017 – Springer. Режим доступу: https://link.springer.com/search?query=Experimental+and+Modeling+Study+on+Reduction+of+Hematite+Pellets+by+Hydrogen+Gas

9. Patisson F. Hydrogen steelmaking. Part 1: Physical chemistry and process metallurgy / F. Patisson, O. Mirgaux,J.–P. Birat // Matériaux & Techniques. – 2021. V. 109. – № 3–4. – P. 303–313. Режим доступу:https://doi.org/10.1051/mattech/2021025

10. Wolfinger T. Analysis of the Usability of Iron Ore Ultra–Fines for Hydrogen–Based Fluidized Bed Direct Reduction — A Review / T. Wolfinger, D. Spreitzer, J. Schenk // Materials 2022, 15, 2687.

Режим доступу: https://doi.org/10.3390/ma15072687

11. Лакомский В. И. Плазменно–дуговой переплав / В.И. Лакомский. – Киев: Техника, 1974. – 335 с.

12. M. NaseriSeftejani.Reaction kinetics of molten iron oxides reduction using hydrogen / M. Naseri Seftejani, J. Schenk // La Metallurgia Italiana. – July 2018. Режим доступу: https://www.researchgate.net/publication/327594827

13. Masab Naseri Seftejani.Thermodynamic of Liquid Iron Ore Reduction by Hydrogen Thermal Plasma / Masab Naseri Seftejani, Johannes Schenk // Metals. – 2018. –8, 1051; DOI:10.3390/met8121051

Режим доступу: https://www.researchgate.net/publication/329566574

14. Saikat Kumar Kuila. Kinetics of hydrogen reduction of magnetite ore fines / Saikat Kumar Kuila, Ritayan Chatterjee, Dinabandhu Ghosh // International journal of hydrogen energy. – 2016. – № 41. – P. 9256–9266.

Режим доступу: https://www.researchgate.net/publication/302555270

15. Isnaldi R. Souza Filho. Green steel at its crossroads: hybrid hydrogen–based reduction of iron ores /Isnaldi R. Souza Filho, Hauke Springer, Yan Ma, Ankita Mahajan, Cauê C. Da Silva,Michael Kulse, Dierk Raabe. – 2022.

Режим доступу: https://arxiv.org/ftp/arxiv/papers/2201/2201.13356.pdf

Popovych Vasyl, Petryk Ivan
(IFNTUOG, Ivano-Frankivsk)
RESEARCH INTERACTION FeTi WITH HYDROGEN
E-mail: iyap@ukr.net

Hydrogen is an attractive energy source in terms of prevalence, environmental friendliness and energy efficiency with its participation. The development of hydrogen energy is limited by the problems of storage and transportation of hydrogen. Binary