

Kinetics of molten iron oxides reduction using hydrogen

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In conventional iron- and steel- making routs, hydrogen is used in molecular state. However, in hydrogen plasma smelting reduction (HPSR), hydrogen is used in plasma state to reduce iron oxide. In this study, the kinetics of molten iron oxide reduction using hydrogen in molecular and plasma state are discussed. HPSR has been established as an alternative to existing iron- and steel-making processes to reduce the emission of CO₂. In HPSR, a H₂-Ar mixture is injected into the plasma arc zone in a plasma reactor. Hydrogen particles become partially atomized and ionized. Thermodynamics calculations show that hydrogen particles in plasma state are strong reducing agents for iron oxides. This study provides an overview for generating hydrogen plasma in an arc plasma reactor and compares the reduction rate of iron oxide using various reducing agents. The results show that hydrogen in the plasma state is the strongest reducing agent. In addition, to increase the reduction rate of iron oxide, the temperature of the hydrogen particles should be increased.

KEYWORDS: HYDROGEN PLASMA – SMELTING REDUCTION– HPSR – IRON OXIDE– PLASMA ARC

INTRODUCTION

The use of coal, coke, and natural gas in iron- and steel-making processes has led to the generation of the greenhouse gas CO₂. The quantity of CO₂ emitted depends on the iron- and steel-making route. The integrated Hyl3-electric arc furnace process route, which produces 1125 kg/ton of hot metal, is the best steel-making route in terms of greenhouse gas emissions [1]. The iron and steel industries produce 7% of the total anthropogenic CO₂ emissions [2]. Hydrogen plasma smelting reduction (HPSR) uses hydrogen to reduce iron oxides to directly produce crude steel products, thus eliminating the use of carbon. Therefore, HPSR is considered a next-generation steel-making process. Hence, understanding the kinetics of this method is important for controlling the process. HPSR provides good reducing conditions by the application of hydrogen and high plasma temperature to intensify the reduction processes; thus, it not only facilitates the production of iron in a one-stage process but also prevents the introduction of carbon in the product, which in turn makes the metallurgical equipment compact [3]. It has been reported that reducing iron ores by hydrogen is 20% cheaper than conventional steel-making processes; moreover, steel produced in this manner is of higher quality and has greater flexibility [4].

In HPSR, plasma is generated by creating an electric arc between a hollow graphite electrode as the cathode and molten iron oxide bath as the anode, with continual input of a mixed gas containing argon and hydrogen. The basic flowsheet of the HPSR process has been presented in our previous study [5]. In the process, argon or nitrogen is used to conduct the current

in the plasma arc; argon is preferred due to its low ionization energy and high conductivity. Hydrogen operates as the reducing agent; hence, a mixture of hydrogen and argon is injected into the arc zone in the reactor through the hollow graphite electrode. Collision of electrons with hydrogen molecules at high temperatures leads to the activation of the hydrogen molecules. The injection of gases through the electrode directly to the arc zone guarantees optimal conditions for atomization and ionization.

Excited hydrogen molecules provide a potentially very useful

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way for the reduction of stable metal oxides. Because monoatomic hydrogen is unstable, the production of pure hydrogen with an industrially usable lifetime is almost impossible. Nevertheless, in plasma arc discharge reactors, mixtures of H and H_2 and hydrogen ions can be produced. Produced metastable mixtures have a suitable lifetime to reduce iron ores [6].

PHYSICAL AND THERMODYNAMIC PROPERTIES OF HYDROGEN THERMAL PLASMA

HPSR consists of a plasma reactor in which the plasma arc formed at the tip of the hollow graphite electrode leads to the atomization and ionization of hydrogen molecules. Plasma arc is formed by the light electrons (negative particles) and heavy hydrogen ions (positive particles), which are two different gases. Among the various ionization processes of atoms, the

dominant ionization process in the electric arc (HPSR process) is collisional ionization by energetic electrons [7].

In HPSR, the arc temperature is between 20000 °C and 25000 °C. Thus, the atomization and ionization of hydrogen molecules take place in the arc zone. In contrast, with increasing distance from the arc, the recombination process becomes more dominant. The rates of ionization and recombination should be balanced by the reciprocal process at thermodynamic equilibrium [7–9]. **Fig. 1** shows the dissociation and ionization of a mixture of 50 mol.% molecular hydrogen and 50 mol.% molecular argon with respect to plasma temperature, as calculated by FactSage™ 7.1 at equilibrium. It is obvious that above 15000°C, the amount of ionized hydrogen (H^+) exceeds the amount of atomized hydrogen (H).

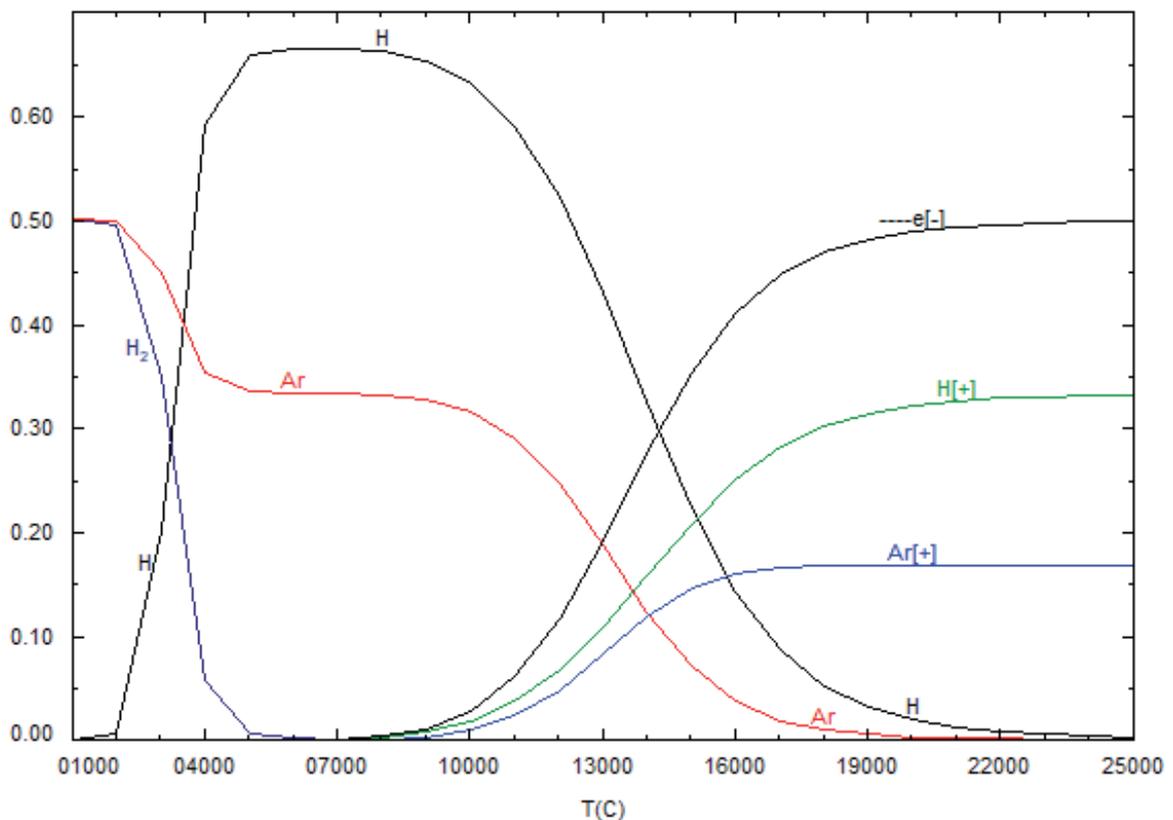


Fig. 1 – Composition of $Ar-H_2$ mixed plasma as a function of temperature (FactSage™ 7.1, Database FactPS)

Various phenomena may occur due to the collision of two particles in plasma. Particles can change their energy or momentum, which in turn can lead to neutral particles getting ionized and ionized particles getting neutral. The dominant collision mechanism for electrons colliding with atoms is elastic scattering. In this mechanism, at first, the electron momentum is changed and then excitation and ionization occur. Similarly, the collision

between ions and atoms is also governed by elastic scattering [9, 10]. During HPSR, almost all types of collisions occur in the arc zone. The amount of energy transferred during collision between electrons and atoms is negligible. In contrast, the kinetic energy significantly changes during atom-molecule collisions [11].

REACTION RATES OF HYDROGEN IONIZATION IN PLASMA STATE

When electrons collide with atoms, the atoms get ionized. The

following equation is used to determine the degree of hydrogen ionization at temperature T:

$$(1) \quad \frac{x^2}{1-x} = \frac{1}{n} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-13.6eV/kT}$$

where $x = n_{r+1}/n_r$ is the degree of ionization, n_r and n_{r+1} are the number densities of atoms in the r and $r + 1$ state, respectively, T is the temperature, h is Planck's constant, k is the Boltzmann constant, and K is the number of hydrogen atoms [7]. Obviously, the ionization fraction sharply increases with increasing temperature.

According to the Maxwell-Boltzmann distribution function, the mean velocity of particles depends on the square root of the temperature [7, 10–12]. Dembovsky [13] reported that the density of the active particles in an electrically insulated surface

and in the absence of an externally applied electric field depends on the particle temperature and the density of the particles. Therefore, there are two ways to increase the number of active hydrogen particles in HPSR: (1) by increasing the injection flow rate of hydrogen gas and (2) by increasing the temperature of the plasma arc.

To calculate the production rate of new electrons per unit volume, the ionization collision frequency is multiplied by the electron density n_e . This source rate S_e of electrons is given by

$$(2) \quad S_e = n_e n_n (\sigma_{ion} v_e)$$

where n_e and n_n are the electron density and neutral atom density, respectively, σ_{ion} is the collision cross-section for electron-impact ionization, and v_e is the electron velocity. In contrast, the rate of recombination is determined by the sink rate. The

value is the inverse of S_e . The following formula shows a good approximation of the ionization rate ($\sigma_{ion} v_e$) of hydrogen atoms by the Maxwellian distribution as a function of electron temperature T_e [7, 14, 14]:

$$(3) \quad (\sigma_{ion} v_e) = \frac{2 \times 10^{-13}}{6 + T_e/13.6} \times (T_e/13.6)^{1/2} \times e^{(-13.6/T_e)} [m^3 s^{-1}]$$

The equation shows that at partial ionization of hydrogen, temperature is the main influencing parameter. In this process, electrons collide with hydrogen atoms.

To obtain the rate of hydrogen ionization, the following reaction is considered:



If the relative velocity of the hydrogen particle H and electron e is V_{HE} and \vec{V}_{HE} is the corresponding collision cross-section for

these two particles, the probability of the collision of an electron with a hydrogen atom is given by

$$(5) \quad dw = n_H \cdot \sigma_{He}(\vec{V}_{He}) \cdot \vec{V}_{He} \cdot dt$$

where n_H is the density of hydrogen atoms. In addition, the probability of total collisions is

$$(6) \quad \frac{dw}{dt} = n_H \cdot n_e \cdot \sigma_{He} \cdot (\vec{V}_{He}) \cdot \vec{V}_{He} = n_H \cdot n_e \cdot k_{He}$$

where n_{He} is the density of electrons and K_{He} is the collision rate or reaction rate [7, 11].

KINETICS OF MOLTEN IRON OXIDE REDUCTION USING HYDROGEN

In HPSR, the plasma arc zone is limited to a cone shape between the tip of the graphite electrode and the surface of the liquid iron oxide. Therefore, only this zone is at the plasma temperature, and it is the preferred area for atomization and ionization. The temperature of the surrounding area decreases with increasing distance from the arc zone. The gas temperature in the freeboard region of the reactor is about 1700 °K. Therefore, it is important that the reduction reactions in the arc zone take place in a short period. Hence, the kinetics of the reduction using hydrogen in the plasma state plays an essential role in this process.

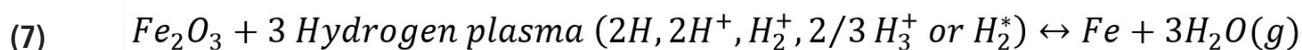
Many studies have evaluated the reduction rate of solid iron oxides in conventional steel-making processes involving hydrogen and other reducing agents. However, research on the kinetics of liquid iron oxide reduction is scarce. A few researchers have evaluated the reduction of iron oxides using hydrogen in plasma state. HPSR is one of the main important topics in terms of reducing liquid iron oxide in a plasma reactor using hydrogen and was proposed by the Chair of Ferrous Metallurgy of Montanuniversitaet Leoben in 1992. A lab-scale plasma facility, equipped with a mass spectrometer to analyze the off gas, was installed at the Chair of Ferrous Metallurgy. The reduction

rates of different iron ores and iron oxides by hydrogen in molecular and plasma states were evaluated previously [15–20]. The results showed that the reduction rate was improved with increasing hydrogen flow rate. In contrast, the hydrogen utilization degree was lower at high flow rates.

Katayama et al. [21] investigated the reduction rate of liquid iron ore by a mixed H_2-H_2O gas to simulate blast furnace slag. Nagasaka et al. [22] reported that the reduction rate of pure liquid iron oxide by hydrogen was very high and gas-phase mass transfer was predominant. The reduction of hematite by microwave-assisted non-thermal hydrogen plasma was studied by Rajput et al. [23]. They indicated that hematite was reduced by excited hydrogen molecules even at temperatures below 573 °K. However, molecular hydrogen could not reduce hematite under the same conditions. The reason was that plasma dissociated and excited hydrogen molecules, which in turn decreased the activation energy from 46 to 5.36 KJ/mol [24].

Mechanism of iron oxide reduction by hydrogen

Plasma smelting technology for the reduction of iron ores has been investigated since the late 1970s [15, 19, 20, 25, 26]. The stoichiometric equation of hematite reduction by hydrogen is given by



For a reaction to take place, the reactants must first collide to cope with the activation barrier. The increase in the temperature of the system increases the number of molecules with sufficient energy to react. The reduction rate is defined by the slowest step of the process, which restricts the overall reaction rate. Kamiya et al. [27] presented a mechanism for iron oxide reduction using hydrogen plasma through the following steps:

- 1- Mass transfer of hydrogen in the gas phase to the reaction zone
- 2- Mass transfer of oxygen through a liquid film from molten iron oxide to the reaction interface
- 3- Adsorption of hydrogen particles at the reaction interface

- 4- Adsorption with dissociation of iron oxide at the reaction interface
- 5- Reduction at the reaction interface and formation of water vapor
- 6- Desorption of water vapor from the reaction interface
- 7- Mass transfer of water vapor from the reaction interface

Hayashi et al. [28] proposed the mechanism of iron oxide reduction using hydrogen in a gas-conveyed system (Fig. 2). In this model, the mass transfer step through the gas flow and interfacial reduction reactions were considered.

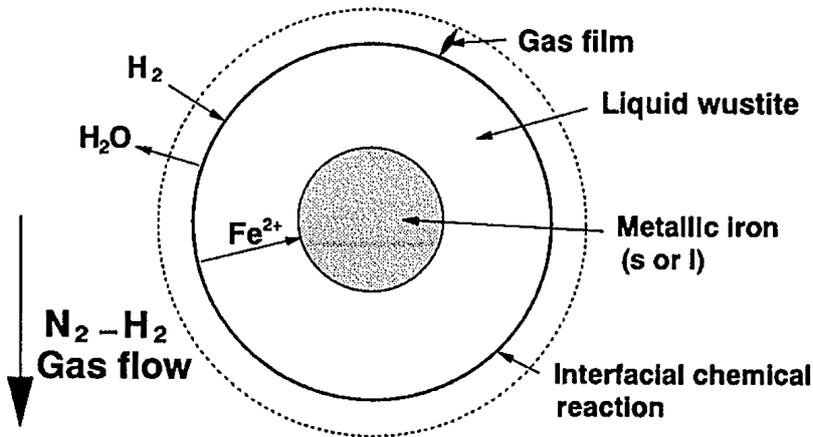


Fig. 2 – Reduction reaction model for a single iron oxide particle [28]

Nagasaka et al. [22] suggested the following limiting steps for the reduction of iron oxide using hydrogen:

1. Mass transfer in gas flow
2. Interfacial reduction reaction
3. Mass transfer of oxygen in the liquid phase to the reaction surface

They represented that the rate of reduction in a gas-liquid system was mainly defined by the chemical reaction at the inter-

face when sufficient flow rate of the reducing agent was used.

IRON OXIDE REDUCTION RATE WITH HYDROGEN

The reduction rate of pure liquid Fe_3O_4 depends on the partial pressure of H_2 in the H_2-Ar mixture. As shown in Fig. 3, the reduction rate is determined by the interfacial chemical reaction rate with respect to hydrogen partial pressure.

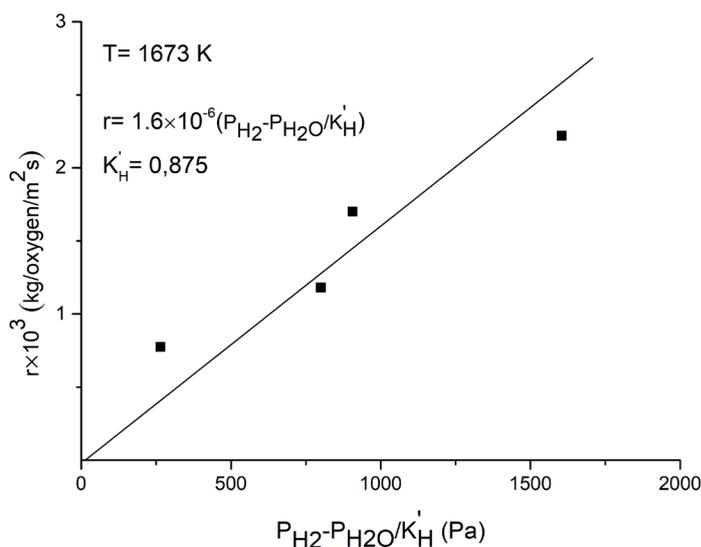


Fig. 3 – Effect of H_2 partial pressure in gas mixture on the apparent chemical reaction rate in the reduction of pure liquid iron oxide using hydrogen at 1673 K [29]

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The reduction rate is given by

$$(8) \quad r = k_a[H_2](P_{H_2} - P_{H_2O}/K'_H) = 1.6 \times 10^{-6}(P_{H_2} - P_{H_2O}/K'_H) \text{ (Pure liquid } Fe_tO \text{ at 1673 K)}$$

where r is the specific reduction rate ($Kg\text{-oxygen}/m^2s$), $K'_a[H_2]$ is the apparent rate constant for hydrogen reduction ($Kg\text{-oxygen}/m^2s Pa$), P_{H_2} and P_{H_2O} (Pa) are the H_2 and H_2O partial pressures, respectively, and K'_H is the gas ratio of (P_{H_2} / P_{H_2O}) at equilibrium with liquid Fe_tO and pure solid iron. For this reaction, the specific reduction rate or apparent rate constant $K'_a[H_2]$ using

hydrogen was $1.6 \times 10^{-6}(Kg\text{-oxygen}/m^2s Pa)$ at 1673 K. As a result, $(P_{H_2} - P_{H_2O}/K'_H)$ was the driving force of the reaction. The following equation shows the reduction rate of liquid iron oxide by CO with consideration for the gas composition and partial pressure of CO :

$$(9) \quad r = k_a[CO](P_{CO} - P_{CO_2}/K'_C) = 1.91 \times 10^{-8}(P_{CO} - P_{CO_2}/K'_C) \text{ (Pure liquid } Fe_tO \text{ at 1673 K)}$$

where $K'_a[CO]$ is the apparent rate constant for CO reduction ($Kg\text{-oxygen}/m^2s Pa$), P_{CO} and P_{CO_2} (Pa) are the CO and CO_2 partial pressures, respectively, and K'_C is the gas ratio of (P_{CO} / P_{CO_2}). The apparent rate constant for hydrogen reduction is approximately two orders of magnitude greater than that for CO reduction. Therefore, the reduction rate of liquid Fe_tO by hydrogen was faster than that by CO .

Hayashi and Iguchi [28] studied the reduction of pure liquid Fe_tO by hydrogen at 1773 °K. In their experiments, very fine Fe_tO particles were reacted with $H_2\text{-}N_2$ mixture in a particle-gas conveyed system. The flow rate and hydrogen concentration were in the range of 0.6–3 NI/min and 5–30 vol%, respectively. They showed that the chemical reaction rate was controlled by P_{H_2} in the gas phase, and the apparent rate constant was reported to be $1.58 \times 10^{-6} (Kg\text{-oxygen}/m^2s Pa)$, which was in good agreement with the results of Nagasaka et al. [29]. Moreover, the reduction rate above the wustite melting point was 13.2 times higher than that in the solid phase.

In HPSR, fine iron oxide is injected into the plasma zone via a hollow graphite electrode that is in contact with partially ionized hydrogen at high temperatures. Therefore, the inflight reduction should be taken into account. Moreover, the most important advantages of HPSR are the use of ionized hydrogen and the high temperatures of the iron ore particles.

Kamiya et al. [27] have constructed a lab-scale plasma furnace for investigating the reduction rate of iron ore, which is shown in Fig. 4. A thoriated tungsten electrode was used as the cathode with consideration of the non-transferred arc attachment. A mixture of hydrogen and argon was injected into the plasma zone via a plasma torch cooled by water. Iron oxide was melted in a 60-mm-diameter water-cooled copper crucible. After complete melting of iron oxide in the crucible, the plasma gas ($H_2\text{-}Ar$ mixture) was then injected into the furnace. The gas flow rate was between 10 and 30 NI/min for up to 75 g of iron oxide and the input DC power was 8.3 kW.

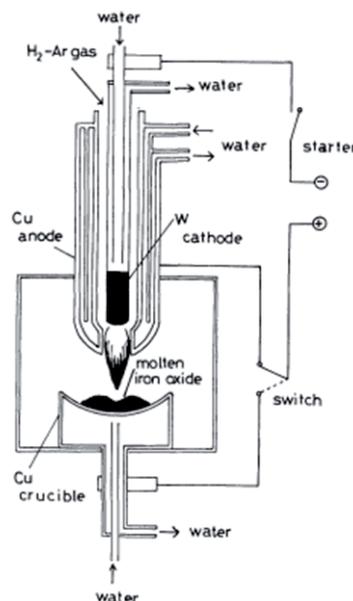


Fig. 4 – Schematic of experimental apparatus [27]

Kamiya et al. [27] reported that the reduction rate of liquid FeO was limited by the chemical reaction between FeO and atomic hydrogen in the plasma arc zone. The reduction reaction took place in the cavity formed on the molten pool surface due to the momentum of the plasma jet gas. Moreover, when sufficient hydrogen was used, the reduction rate was independent of the flow rate. Their results were in agreement with previous results [25, 27], except for the effect of hydrogen concentration on hydrogen utilization. They showed that the hydrogen utilization degree was constant at about 44% for hydrogen concentrations between 10 and 30 vol% in the H_2 -Ar mixture and was about 60% at hydrogen concentration lower than 10 vol% [27]. However, Badr et al. [16] reported that with increasing hydrogen concentration, the degree of utilization decreased and the maximum utilization was achieved at a hydrogen concentration of 26 vol%. A higher degree of hydrogen utilization at a low concentration of H_2 was in a good agreement with the results of Nakamura et al. [30]. Nakamura et al. [30] mentioned that the reduction rate might be improved by the separation of slag from the reduced iron. This behavior was also confirmed by Lemperle [25], who showed that a higher utilization degree was obtained at lower H_2 concentrations due to the lower rate of recombination of hydrogen particles in plasma state.

Effect of basicity on reduction rate

In HPSR, the temperature and basicity of the slag are the parameters influencing the reduction rate. Partial solidification of the slag leads to a decrease in the reduction rate because of limited oxygen transport to the reaction surface.

Badr [16] experimentally assessed the effect of slag basicity on the reduction rate; however, no linear correlation was found. Further, at a high CaO content, the hydrogen utilization degree decreased. Kamiya et al. [27] also did not observe any obvious changes in the reduction rate on varying the basicity from 0 to 2.

Nagasaka et al. [24] studied the effect of additives such as CaO , Al_2O_3 , and TiO_2 on the reduction rate of liquid FeO by hydrogen at different flow rates of H_2 -Ar mixture. They observed that an increase in the gas flow rate improved the reduction rate of iron oxide, i.e., the flow rate played an important role in these binary slags. As a result, the mass transfer process was the rate-limiting step in the gas phase.

Comparison of iron oxide reduction rates with hydrogen by various researchers

Fig. 5 shows the reduction rate of FeO by hydrogen in solid and liquid states and at the melting point of FeO reported by different studies.

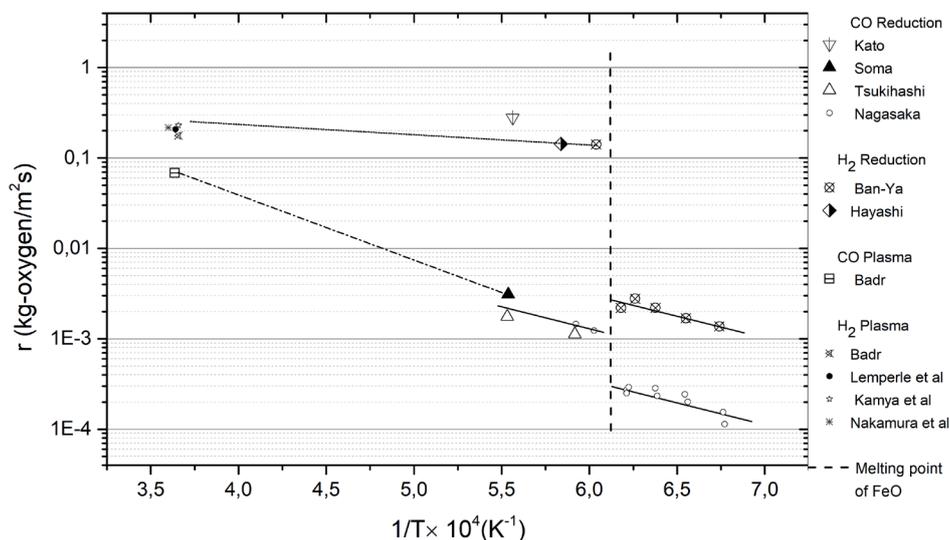


Fig. 5 – Specific reduction rates of molten FeO and wustite by pure H_2 and CO at various temperatures [16]

As can be seen, the reduction potential of hydrogen increased significantly with respect to that of the solid phase just above the FeO melting point. However, above the melting point, the

logarithms of the reduction rate increased linearly with increasing the temperature up to the plasma temperature.

Comparison of reduction rates of molten iron oxide by hydrogen, solid carbon, Fe-C melt, and CO

In terms of the reduction of molten iron oxide by CO, Nagasaka et al. [22] represented most of the related studies [31–33] in a plot for comparison. The results were in good agreement with each other, except for those of Kato et al. [16], which were later corrected by Soma [31]. Nagasaka et al. [22] showed that the reduction rate of FeO by CO increased by almost one order of magnitude just above the melting point.

Many researchers have studied the reduction of molten FeO by solid carbon [32, 34–36]. One of the main results was that the reduction rate of pure liquid FeO by solid carbon was signifi-

cantly affected by temperature. Moreover, the reduction rate of liquid iron oxide by Fe–C was significantly higher than that by solid carbon up to 1893 K.

A comparison of the reduction rates of liquid iron oxide by hydrogen, solid carbon, Fe–C melt, and CO is represented in Fig. 6. The reductions by H₂ and CO were referred to the interfacial chemical reaction. In contrast, for the reductions by solid carbon and Fe–C melt, the overall rates were considered. Consequently, the reduction rate by hydrogen was one or two orders of magnitude higher than those by the other reductants [22].

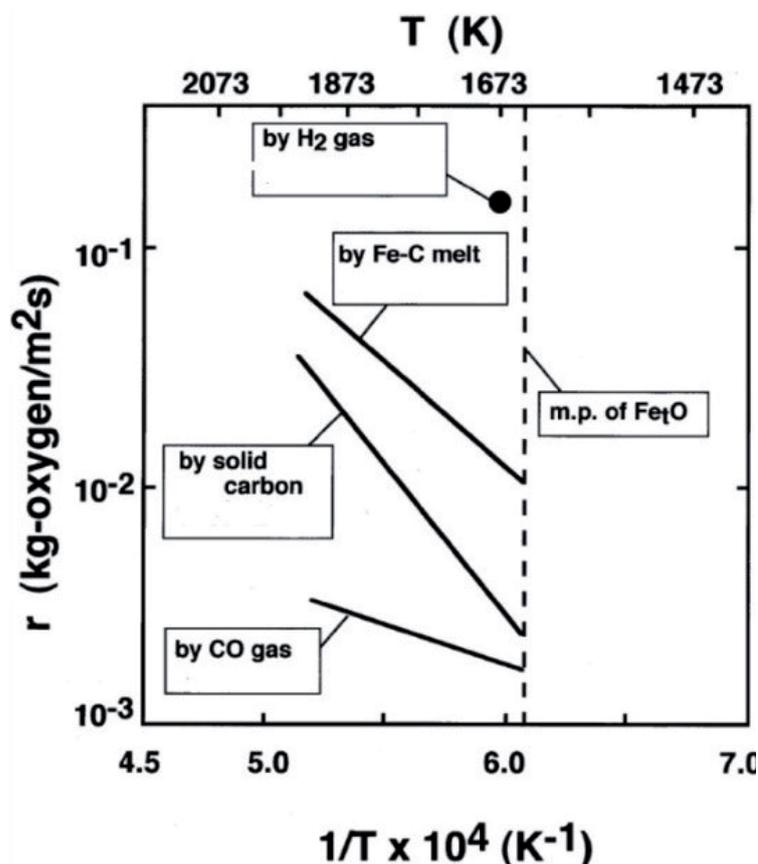


Fig. 6 – Comparison of reduction rates of pure liquid iron oxide by solid carbon, Fe–C melt, CO, and H₂ [22]

Summary and conclusion

Thermodynamic calculations at equilibrium show that hydrogen and argon are ionized at plasma arc temperatures. Moreover, the hydrogen species in plasma state is the strongest reducing agent in terms of Gibbs free energy. The reduction abilities of different hydrogen species can be expressed in the following order: $H^+ > H_2^+ > H_3^+ > H > H_2$.

To evaluate the reduction of iron oxide by hydrogen, the reduction rate should be taken into account and the ionization degree of the hydrogen particles should be assessed. To cover those, the main parameters

influencing the ionization degree are analyzed. It is found that the ionization degree increases with increasing temperature and number density of the hydrogen particles.

Finally, the reduction rates of iron oxides by various reducing agents are studied and the reduction abilities are graphically compared. Consequently, the iron oxide reduction rate by hydrogen is one or two orders of magnitude higher than those by other reductants.

REFERENCES

- [1] Lisienko VG, Lapteva AV, Chesnokov YN, Lugovkin VV. Greenhouse-gas (CO₂) emissions in the steel industry. *Steel Transl.* 2015; 45(9):623–6.
- [2] Kim Y, Worrell E. International comparison of CO₂ emission trends in the iron and steel industry. *Energy Policy* 2002; 30(10):827–38.
- [3] Fridman AA. *Plasma chemistry*. Cambridge, New York: Cambridge University Press; 2008.
- [4] Hiebler H, Plaul JF. Hydrogen plasma- smelting reduction- an option for steel making in the future [METABK] 2004 [cited 2016 Jan 20]; 43(0543-5846):155–62.
- [5] Naseri Seftejani M, Schenk J, editors. *Fundamentals of hydrogen plasma smelting reduction (HPSR) of iron oxides, a new generation of steelmaking processes*. Conference proceedings; 2018. (Iron and steel Society).
- [6] Robino CV. Representation of mixed reactive gases on free energy (Ellingham-Richardson) diagrams. *Metall and Materi Trans B* 1996; 27(1):65–9.
- [7] Keidar M, Beilis I. *Plasma Engineering: Applications from aerospace to bio and nanotechnology*. San Diego: Elsevier Science; 2013.
- [8] Piel A. *Plasma physics: An introduction to laboratory, space, and fusion plasmas / Alexander Piel*. Heidelberg: Springer; 2010.
- [9] Janev RK, Reiter D, Samm U. *Collision processes in low-temperature hydrogen plasmas: 1* Institut für Plasmaphysik, Forschungszentrum Jülich GmbH, EURATOM Association, Trilateral.
- [10] Lichtenberg AJ, Lieberman MA. *Principles of plasma discharges and materials processing*. 2nd ed. Hoboken, N.J., Chichester: Wiley-Interscience; 2005.
- [11] Feinman J. *Plasma technology in metallurgical processing*. USA: Iron and steel Society; 1987.
- [12] Freemire B, Hanlet PM, Torun Y. Determining electron temperature and density in a hydrogen microwave plasma. *Journal of Thermophysics and Heat Transfer* 1996; 10(3):426–35.
- [13] Dembovsky V. How the polarity of a surface reacting with a low temperature plasma affects the thermodynamic variables in metallurgical reactions. *Achta Physic Slovenia* 1984; 34(1):11–8.
- [14] Goldston RJ, Rutherford PH. *Introduction to plasma physics*. Bristol: Institute of Physics Pub; 1995 (2000 [printing]).
- [15] Plaul JF. *Schmelzreduktion von hämatitischen Feinerzen im Wasserstoff-Argon-Plasma [Doktoral]*. Leoben, Austria; 2005.
- [16] Badr K. *Smelting of iron oxides using hydrogen based plasmas [Doctoral Dissertation]*. Leoben, Austria.
- [17] Badr K, Bäck E, Krieger W. Reduction of iron ore by a mixture of Ar-H₂ with CO and CO₂ under plasma application. 18th International Symposium on Plasma Chemistry 2007.
- [18] Kirschen M, Badr K, Pfeifer H. Influence of direct reduced iron on the energy balance of the electric arc furnace in steel industry. *Energy* 2011; 36(10):6146–55.
- [19] Bäck E. *Schmelzreduktion von Eisenoxiden mit Argon-Wasserstoff- Plasma [Doctoral Dissertation]*. Leoben, Austria; 1998.
- [20] Sormann A. *Untersuchungen zur Schmelzreduktion von Eisenoxiden mit Wasserstoff als Reduktionsmittel [Doktoral Disserta-*

- tion]. Leoben, Austria; 1992.
- 21] Katayama, H., S. Taguchi, and N. Tsuchiya H, Taguchi s, Tsuchiya N. Reduction of iron oxide in molten slag with H₂ gas. ISIJ Int. 1982 [cited 2016 Jan 20]; 68:2279–86.
 - 22] Nagasaka T, Hino M, Ban-ya S. Interfacial kinetics of hydrogen with liquid slag containing iron oxide. Metall and Materi Trans B 2000; 31(5):945–55.
 - 23] Rajput P, Bhoi B, Sahoo S, Paramguru RK, Mishra BK. Preliminary investigation into direct reduction of iron in low temperature hydrogen plasma. Ironmaking & Steelmaking 2013; 40(1):61–8.
 - 24] Sabat KC, Rajput P, Paramguru RK, Bhoi B, Mishra BK. Reduction of oxide minerals by hydrogen plasma: An Overview. Plasma Chem Plasma Process 2014; 34(1):1–23.
 - 25] Weigel A, Lemperle M, Lyhs W, Wilhelmi H. Experiments on the reduction of iron ores with an argon hydrogen plasma. ISPC-7 Eindhoven 1985:1214–9.
 - 26] Gilles HL, Clump CW. Reduction of iron ore with hydrogen in a direct current plasma jet. Ind. Eng. Chem. Proc. Des. Dev. 1970; 9(2):194–207.
 - 27] Kamiya K, Kitahara N, Morinaka I, Sakuraya K, Ozawa M, Tanaka M. Reduction of molten iron oxide and FeO bearing slags by H₂-Ar plasma. ISIJ Int. 1984; 24(1):7–16.
 - 28] Hayashi S, (None), Iguchi Y. Hydrogen reduction of liquid iron oxide fines in gas-conveyed systems. ISIJ International 1994; 34(7):555–61.
 - 29] Ban-ya S, Ighuchi Y, Nagasaka T. Rate of reduction of liquid wustite with hydrogen. tetsu-to-hagane; 70:1689–96.
 - 30] Nakamura Y, Ito M, Ishikawa H. Reduction and dephosphorization of molten iron oxide with hydrogen-argon plasma. Plasma Chem Plasma Process 1981; 1(2):149–60.
 - 31] Soma T. Smelting reduction of iron ore. Bulletin of the Japan Institute of Metals 1982; 21(8):620–5.
 - 32] Tsukihashi F, Amatatsu M, Soma T. Reduction of molten iron ore with carbon. ISIJ Int. 1982 [cited 2016 Jan 21]; 22:688–95.
 - 33] Nagasaka T, Iguchi Y, Ban-ya S. Effect of additives on the rate of reduction of liquid iron oxide with CO. tetsu-to-hagane 1989; 75(1):74–81. Available from: URL: <http://ci.nii.ac.jp/lognavi?name=nels&lang=jp&type=pdf&id=ART0001818203>.
 - 34] Takahashi K, Amatatsu M, Soma T. Reduction of Molten Iron Ore with Solid Carbon. tetsu-to-hagane 1975 [cited 2016 Jan 21]; 61:2525–30.
 - 35] Sasaki Y, Okamoto Y, Soma T. Kinetics of Reaction between Iron Oxide Slags and Solid Carbon. ISIJ International 1978; 64(3):367–75. Available from: URL: <http://ci.nii.ac.jp/lognavi?name=nels&lang=jp&type=pdf&id=ART0001787448>.
 - 36] Sato A, Aragane G, Kamihira K, Yoshimatsu S. Reduction Rate of Molten Iron Oxide by the Solid Carbon or the Carbon in Molten Iron. tetsu-to-hagane 1987 [cited 2016 Jan 21]; 73:812–9.