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Reduction of Oxide Minerals by Hydrogen Plasma: An Overview

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Abstract Carbothermic reduction of oxide minerals is one of the major routes to obtain the corresponding metals. This process produces a lot of CO_2, which is responsible for greenhouse effect. Alternatively, hydrogen plasma containing hydrogen in atomic, ionic, and excited states can reduce almost every metal oxide even at lower temperatures. Besides this advantage, plasma processing also offers kinetic advantages. Further, hydrogen-water cycle does not pose any environmental problems. However, reduction of metal oxides in hydrogen plasma is not so straightforward—there are issues relating to introduction of material into the plasma zone, residence time, reverse reaction, and scale-up that must be resolved—yet, it holds the key to future environmental challenges particularly with respect to CO_2 emission. This paper provides an overview of reduction of oxide minerals by hydrogen plasma. The influences of various reaction conditions particularly with respect to reduction of oxides are discussed and some aspects of both thermal and non-thermal cold plasma linking oxidative as well as dissociative reduction are presented.

Keywords Hydrogen plasma · Thermal plasma · Non-thermal plasma · Oxide minerals

Introduction

At present, global crude steel production has touched 1,500 million tons per annum [1] followed by other base metals and alloys. Most of the metals such as iron, aluminium, silicon, manganese, chromium, nickel, titanium, vanadium, etc., are extracted from oxide minerals. The extraction involves carbon as reductant in one form or other which has limitations of (future) supply and environmental pollution. Needless to mention that CO_2

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production from steel alone constitutes 5 % of total CO_2 generation [2]. After the commitment of participating countries to reduce CO_2 in Kyoto agreement, it became necessary to find innovative technologies to decrease CO_2 emissions produced by the steel industry. The World Steel Association, whose members represent about 85 % of world steel producers, is working through its "CO_2 breakthrough programme" to reduce steel emissions. One of the leading activities relating to CO_2 generation is European Union's Ultra Low CO_2 Steelmaking (ULCOS) initiative. ULCOS is an effort to use raw materials in powder form for making pig iron, hence avoiding the regular ore and coke agglomeration processes. The aim is to cut CO_2 emission at least to 50 % level of current emission by 2,050 [3]. Researchers are also motivated to think about alternative reductants in place of carbon. Both of the above drawbacks i.e., supply of coke and CO_2 emission can be resolved by using hydrogen. Thus hydrogen stands as the strongest candidate for reduction of metal oxides [4–6]. The merits of hydrogen reduction vis-à-vis carbon reduction are twofold: first, the combustion product is steam or water which is non-pollutant, and second, its consumption is less as compared to carbonaceous reductant as shown in Table 1 [7]. Theoretically, to produce one tonne of pure iron, about 650 Nm^3 of hydrogen is required which is equivalent to 6.5 GJ/tonne and it is of the same order of magnitude as the minimum energy demand (6.8 GJ/tonne) when coke is used [8]. It has been found that steel produced by hydrogen can be 20 % cheaper than the conventional steel making routes and the steel produced in this manner would be of higher product quality and flexibility [9].

Thermodynamics of Hydrogen Plasma Reduction

Thermodynamics and kinetics principles constitute towards potential pathways of the production process. The reaction of interest is the reduction of a metal oxide (MO) by hydrogen plasma. Hydrogen gas is supplied in molecular form to the plasma site where the reduction of metal oxide takes place. Plasma changes molecular hydrogen gas to atomic, ionic, or vibrationally activated and other excited forms. The reaction in its general form is

$$\mathrm{MO}_x + \mathrm{x}H_2(\mathrm{g}) = \mathrm{M} + \mathrm{x}H_2\mathrm{O}(\mathrm{g}) \quad \Delta\mathrm{G}_1 > 0 \tag{1}$$

where MO and M represent metal oxide and metal respectively; ΔG is the Gibbs free energy change.

Activation of molecular hydrogen gas by plasma is represented as

$$\mathrm{H}_2(\mathrm{g}) = \mathrm{Hydrogen\,Plasma}(2\mathrm{H}/2\mathrm{H}^+/2\mathrm{H}^{2+}/2\mathrm{H}^{3+}/\mathrm{H}_2^*) \quad \Delta\mathrm{G}_2 \gg 0 \tag{2}$$

Thermodynamic coupling of (1)—(2) leads to

$$\begin{gathered}\mathrm{MO}_x + \mathrm{xHydrogen\,Plasma}(2\mathrm{H}/2\mathrm{H}^+/2\mathrm{H}^{2+}/2\mathrm{H}^{3+}/\mathrm{H}_2^*) = \mathrm{M} + \mathrm{x}H_2\mathrm{O}(\mathrm{g}) \\ \Delta\mathrm{G}_3 = \Delta\mathrm{G}_1 - \mathrm{x}\Delta\mathrm{G}_2 < 0\end{gathered} \tag{3}$$

Table 1 Balance of reductant and product in case of reduction of hematite to iron

Reaction	C	CO	CO_2	H_2	H_2O
$Fe_2O_3 + 3C = 2Fe + 3CO$	36	84			
$Fe_2O_3 + 3/2C = 2Fe + 3/2CO_2$	18		66		
$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O$				6	54

(Tons per 112 tons of Fe [7])

Spontaneity or feasibility of a reaction is established by its free energy change. For a reaction to be spontaneous, the free energy change should be negative. The Gibbs free energy change (ΔG) for reduction of metal oxides with hydrogen plasma becomes negative from positive or more negative even at lower temperatures. It becomes clear from the Ellingham diagram where the standard Gibbs free energy data of oxides is plotted as a function of temperature [9]. The diagram provides an estimate of how changes in temperature, pressure, and composition, affect the relevant chemical equilibrium of oxides and thereby providing clues as to the stability as well as possibility of reduction of oxides. Figure 1 shows the Ellingham diagram for metal-oxide conversion as MO–M, H_2O–H_2, H_2O–H and H_2O–H^+ lines [9–11]. The H_2O–H_2 line lies between the MO-M lines indicating that molecular hydrogen can reduce only those metal oxides which lie above it but it cannot reduce the metal oxides which are lying below it. Interestingly, the H_2O–H and H_2O–H^+ lines lie well below all the metal oxide-metal lines. This shows that theoretically, ΔG° values of H_2O–H and H_2O–H^+ lines are 3 times and 15 times lower than H_2O–H_2 line respectively [9]. This factor shows the advantage of using hydrogen plasma (which consist of monoatomic hydrogen, ionic hydrogen, and vibrationally excited H_2 molecules) to reduce oxide minerals for production of metals and alloys.

Role of Monoatomic Hydrogen

Monoatomic hydrogen provides potentially a useful means for reduction of extremely stable oxides because the H_2O–H line lies below most of the metal oxides in the Ellingham diagram (Fig. 1). The equilibrium partial pressure of molecular/atomic hydrogen required

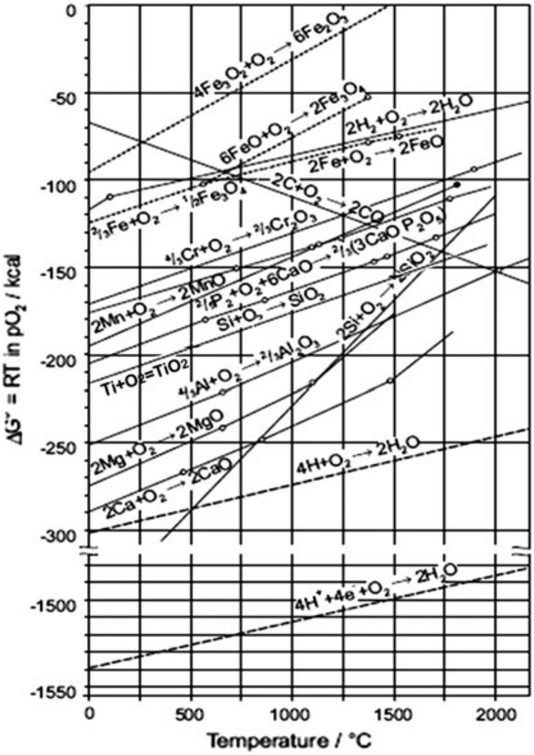

Fig. 1 Ellingham diagram for different oxides [9–11]

for the reduction of metal oxides with hydrogen is determined from the equilibrium constant ($K = P_{H2O}/P_{H2}$). Based on the available data [9–11], the lines corresponding to the equilibrium partial pressure of molecular hydrogen versus temperature and atomic hydrogen versus temperature for reduction of iron oxides (the reactions mentioned in the graph) can be drawn [7]. The equilibrium partial pressure of atomic hydrogen versus temperature for reduction of iron oxides is shown in Fig. 2. It is concluded that unlike the case with molecular hydrogen, the equilibrium partial pressure of atomic hydrogen for these reactions decreases with decrease in temperature. These conditions favor production of direct reduction of oxides using non-thermal hydrogen plasma at low temperatures.

Rouine [12] calculated the standard Gibbs free energy change per mole of H_2O ($\Delta G°_f$) produced for complete reduction of metal oxides with molecular hydrogen and atomic hydrogen at 1,000 K. The corresponding data are shown in Table 2, in order of ease of reducibility (e.g., FeO is more easily reduced than K_2O). The positive values for $\Delta G°_f$ indicate that these oxides will not be significantly reduced by molecular hydrogen at 1,000 K. However, in the presence of atomic hydrogen, reduction of these oxides is thermodynamically favoured at this temperature. The temperature required for a spontaneous reduction is significantly lowered in the presence of atomic hydrogen (i.e., $\Delta G°_f$ becomes negative even at low temperature as shown later in Eq. 10). Bergh [13] determined the reduction temperatures of oxides by molecular hydrogen in electrodeless discharge plasma. He found that the reduction temperature by atomic hydrogen is substantially lower than molecular hydrogen and the corresponding data are shown in Table 3.

Although, the equilibrium partial pressure of atomic hydrogen (H) decreases with decrease in temperature, atomic hydrogen is unstable relative to molecular hydrogen (H_2). Moreover pure H atmosphere having usable lifetime cannot be realized. However, mixtures of H and H_2 with varying fractions of H can be produced. These metastable mixtures have lifetimes that may be applicable to reduction of metal oxides. In order to assess the utility of such mixtures for metal oxide reduction, Robino et al. [14] developed a means to determine the equilibrium between mixtures of H and H_2 and various metal–metal oxide systems. The H and H_2 equilibria are described as follows:

$$2H_2 + O_2 = 2H_2O \quad \Delta G_1^0 = -492.9 + 0.1096T \tag{4}$$

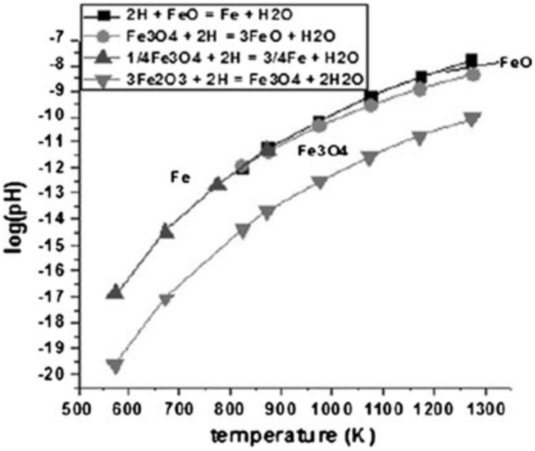

Fig. 2 Temperature–partial pressure position with respect to reduction reactions [7]

Table 2 The change in standard state Gibbs energy per mole of H_2O produced for the complete reduction of the given oxide with either molecular or atomic hydrogen at 1,000 K [5, 12]

Standard state gibbs free energy change (T = 1,000 K)		
Oxides	Reduction with H_2 (kJ/mol O_2)	Reduction with H (kJ/mol O_2)
FeO	12.328	−287.396
K_2O	12.849	−286.875
Na_2O	68.360	−231.364
Cr_2O_3	87.536	−212.187
MnO	114.173	−185.551
SiO_2	164.156	−135.568
TiO_2	178.961	−120.763
$A1_2O_3$	245.991	−53.733
MgO	284.092	−15.632

Table 3 Reduction temperatures of oxides in molecular and atomic hydrogen [13]

Oxides	Colour change (due to reduction) in H_2 (°C)	Colours change (due to reduction) in H (°C)
MoO_3	610	43
GeO_2	560	35
WO_3	535	25
SnO_2	490	100
Fe_2O_3	310	40
PbO	300	25
Cu_2O	265	25
NiO	250	62
CuO	140	25

$$4H = 2H_2 \Delta G_2^0 = -875.61 + 0.21205T \quad (5)$$

$$4H + O_2 = 2H_2O \ \Delta G_3^0 = -1368.51 + 0.3267T \quad (6)$$

Assuming that the hydrogen gas mixture consists of only H, and H_2, and also assuming that the mixture obeys the ideal gas law i.e., $\frac{p_H}{p_{H_2}} = \frac{n_H}{n_{H_2}}$where p and n represent the partial pressure and the number of moles of the components respectively, the mixture of H and H_2 react with oxygen of metal oxide to form water vapour according to the following reaction:

$$n_H H + n_{H_2} H_2 + \left(\frac{n_H}{4} + \frac{n_{H_2}}{2}\right) O_2 = \left(\frac{n_H}{2} + n_{H_2}\right) H_2O \quad (7)$$

Let the mole fraction of H in the mixture is n, so that

$$n = \frac{n_H}{(n_H + n_{H_2})}$$

$$n_{H_2} = \frac{n_H(1 - n)}{n} \quad (8)$$

Combining Eqs. 1 and 2, we get

$$\frac{4n}{2-n}H + \frac{4(1-n)}{2-n}H_2 + O_2 = 2H_2O \tag{9}$$

where ΔG for this reaction is calculated from ΔG_1^0 and ΔG_3^0 as

$$\Delta G_4^0 = \frac{1}{2-n}[-985.75 - 382.75n + (0.21924 + 0.10242n)T] \tag{10}$$

For any metal oxide, Me_xO_y the following reaction holds

$$\frac{2x}{y}Me + O_2 = \frac{2}{y}Me_xO_y \tag{11}$$

and the free energy change for this reaction is ΔG_5^0. For metal oxide reduction by a mixture of H and H_2, the reaction can be represented by

$$\frac{4n}{2-n}H + \frac{4(1-n)}{2-n}H_2 + \frac{2}{y}Me_xO_y = 2H_2O + \frac{2x}{y}Me$$

The free energy change for this overall reduction reaction is $\Delta G = \Delta G_4^0 - \Delta G_5^0$

$$\Delta G = \frac{1}{2-n}[-985.75 - 382.75n + (0.21924 + 0.10242n)T] - \Delta G_5^0$$

Figure 3 shows the effect of presence of atomic hydrogen with molecular hydrogen on standard free energy of hydrogen plasma. The figure shows the variation of free energy for the reaction $[4n/(2-n))]H + [4(1-n)/(2-n)]H_2 + O_2 = 2H_2O$ with increase in atomic hydrogen mole fraction (i.e. *n*) whose value changes from 0 to 1 with increments of 0.2. For molecular hydrogen where no atomic hydrogen is present (i.e. $n = 0$), the reaction becomes $2H_2O + O_2 = 2H_2O$ and ΔG_4^0 calculated from Eq. 10 by putting $n = 0$ is shown in Fig. 3. It is observed that with increase in *n*, there is a clear decrease in ΔG_4^0 making the reduction of metal oxide more feasible.

Role of Ionic Hydrogen

In the hydrogen plasma, monoatomic hydrogen as well as ionic hydrogen species are present. Though the density of ionic hydrogen is less, its reduction potential is much higher. According to Zhang et al. [15], the main chemically active species in hydrogen plasma at moderate pressures are H, H^+, $H_2^+$and H_3^+. The Gibbs free energies for H_2O generated from reactions of different hydrogen species with oxygen are plotted in Fig. 4. It can be seen from the plot that the order of the reduction ability for these species is $H^+ > H_2^+ > H_3^+ > H$. Zhang et al. [16] calculated the free energies for reduction of hematite by different chemically active species, which is shown in Fig. 5. If the diffusion of hydrogen in the metal layer is not the rate limiting step, then the reduction process is determined by the nature of the active species and their concentration ahead of the surface of the specimen.

Role of Vibrationally Excited Hydrogen Molecules

In addition to the atomic and ionic species, plasma also contains ro-vibrationally excited molecules. The ro-vibrationally excited molecules play an essential and extremely

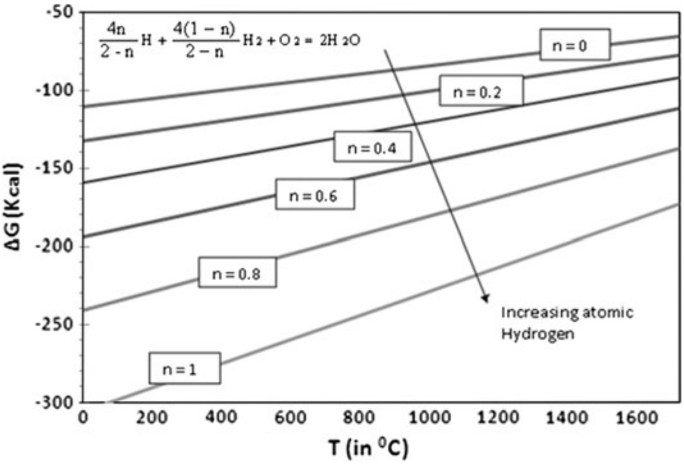

Fig. 3 The temperature variation of the standard free energy for the reaction [4n/(2−n))]H + [4(1−n)/(2−n)]H_2 + O_2 = $2H_2O$

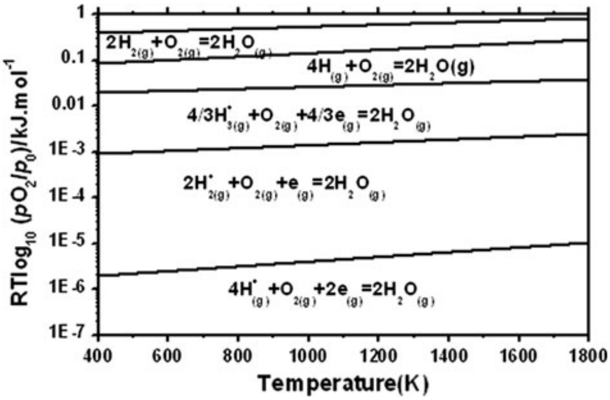

Fig. 4 ΔG^0- T curves for H_2O generated from different chemically active hydrogen species [15]

important role in plasma physics and chemistry of molecular gases [17]. This is primarily due to the following facts:

1. The largest portion of discharge energy (often more than 95 %) in molecular gases usually transfers from plasma electrons primarily to induce molecular vibrations and only then it transfers to different channels of relaxation and chemical reactions [17].
2. The molecular reactions that involve ro-vibrationally excited molecules can be much more efficient compared to reactions with ground state molecules. This increased reactivity is caused by the extra energy stored in rotation and vibration of excited molecules. Due to this extra stored energy, endothermic molecular processes can be enormously enhanced, which is important in a wide variety of applications [18]. The reduction of metal oxides is typically endothermic process. The extra internal energy associated with the vibrationally excited molecules which participate in endothermic reactions transform into translational energy of products [17].

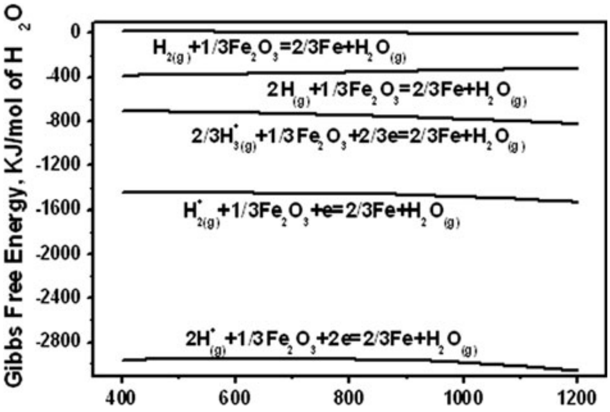

Fig. 5 ΔG^0-T curve for reduction of hematite with different chemically active hydrogen species [16]

3. Several molecules such as H_2, N_2, CO and CO_2 can maintain vibrational energy without relaxation for a relatively longer time. Such vibrational energy results in accumulation of fairly large amounts of energy that can selectively be used in chemical reactions [17].
4. Fortunately, not only can the reduction be made feasible at low temperature in hydrogen plasma but also it can be stimulated by the vibrationally excited hydrogen molecules through their surface dissociation [7, 19].

Role of the Charge Polarity on Thermodynamics

The reduction processes occur at the plasma-substrate/pellet/powder interface where the reducing gas is in the plasma state. The plasma which conducts electricity is in contact with the processed material which is in solid or liquid state. Clearly then the charge polarity must play an important role to attract the desired species from plasma region to the interface where the desired reactions take place. Dembovsky [20] studied the effect of external applied electric field and reported that the charged material attracts particles of opposite polarity and repels particles possessing its own polarity. Clearly, a positively charged surface will attract electrons, but repel positive ions. Therefore, the particles reacting with that surface would be neutral atoms and molecules. On the contrary, a negatively charged surface will repel electrons and hence it would react only with positive ions and electrically neutral atoms and molecules. This aspect is quite important from a practical standpoint.

Dembovsky [20] also reported the effect of polarity of the reacting surface on the thermodynamics, when the surface is reacting with low temperature hydrogen plasma. Figure 6 shows the changes in the standard free energy, $\Delta G°$, at various temperatures of the reacting surface of iron oxide when it is reduced by hydrogen at 10,000 K, in a reaction described as given below.

$$FeO + xH_2 + yH + zH^+ + ze^- \rightarrow Fe + H_2O \tag{13}$$

where x, y and z represent the mole fractions of the corresponding species reaching the reacting surface. Dembovsky [20] demonstrated as shown in Fig. 6, that a positive polarity of the reacting surface reduces the thermodynamic potential of the above reaction in comparison to the case with a neutral reacting surface. Conversely, in case of the surface with negative polarity, the reaction proceeds much faster i.e., ΔG° is more negative. Similar results have been reported by Zhang et al. [16] as will be discussed later.

Kinetics

For a chemical reaction to occur, the reacting particles with enough kinetic energy must first collide to overcome the activation barrier. In the context of plasma-metal oxide interaction, the role of ro-vibrationally excited hydrogen molecules has been emphasized in literature [12, 22, 80]. The ro-vibrationally excited molecules can inherit an internal energy up to 4.5 eV stored in rotation and vibration [22]. They transfer their internal energy to other molecules and atoms in the gas phase by inelastic collisions and chemical reactions. As a result, the internal energy of the reacting species increases and the activation barrier decreases making the reaction easier.

A schematic diagram of the activation energy profile for reduction of oxides with different hydrogen species is shown in Fig. 7 [21]. As shown in the figure, reduction of metal oxide to metal by molecular hydrogen may proceed at high temperatures. However, high activation energy actually prevents the reduction from occurring. Hydrogen can be excited to active states (atomic or ionic) and the energy of excited species remains high. The activation energy (E_2 and E_3) of reactions with active hydrogen species are lower than

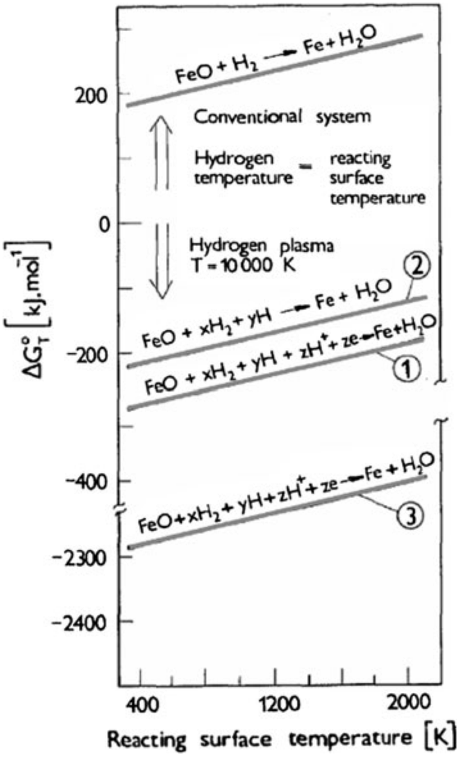

Fig. 6 ΔG° versus surface temperature for FeO reduction by hydrogen plasma [20], *1*-no applied electric field, *2*- surface with positive polarity, *3*- surface with negative polarity

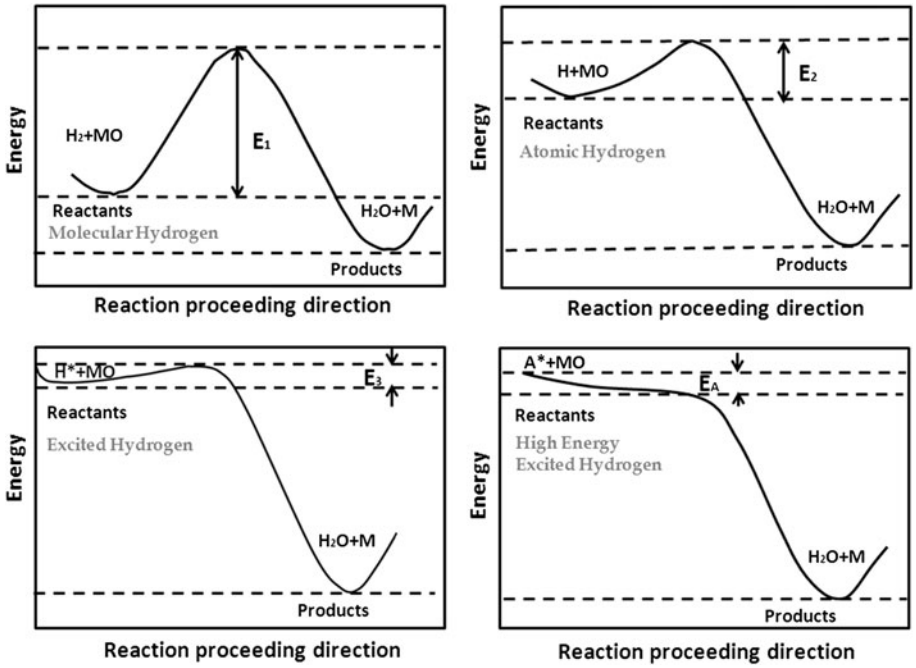

Fig. 7 Schematic diagram of activation energy for reduction of metal oxides with different hydrogen species

the one (E_1) with hot molecular hydrogen. When the active species are of much higher energy, the activation energy (E_A) may be zero or negative.

Rajput et al. [7] carried out solid state reduction of hematite by hydrogen in absence and presence of plasma. Due to the presence of plasma, the activation energy decreased from 46 to 5.36 kJ/mol probably due to ro-vibrationally excited hydrogen molecules. They also reported that vibrationally excited hydrogen molecules stimulate the chemical processes through their surface dissociation and diffusion of hydrogen atoms into the crystal structure, thereby increasing the rate of reduction. Similarly, Badr et al. [29] also carried out reduction of hematite under liquid state and reported a decrease in activation energy by the presence of plasma.

Apart from affecting the gas phase chemistry, the active species also affect the plasma-surface interactions. The surface chemical processes (e.g., reduction of metal oxides by hydrogen plasma) are strongly dependant on fluxes and energies of incoming active species to the surface. The vibrational-translational relaxation of the active species is much faster on metal oxide surface than that in gas phase. This relaxation of the active species causes overheating of the surface. This can stimulate the surface oxide reduction processes further while keeping the gas temperature low.

Reduction of Oxides

Conventional approaches in extractive metallurgy for reduction of metals from their oxides generally include multiple stages and require high temperatures, which merit application of

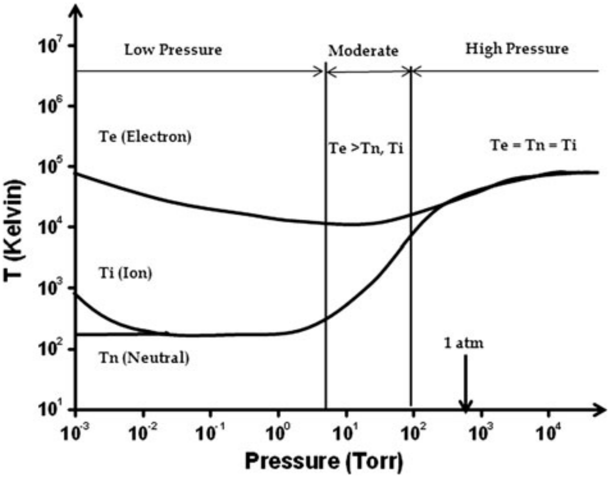

Fig. 8 The temperature of electrons and heavy particles in the plasma as a function of plasma pressure

hydrogen plasma. Hydrogen plasma not only provides improved reducing condition but also provides high plasma temperature to intensify the reduction processes, thereby enabling the possibility of carrying out one stage processes which in turn make the metallurgical equipment smaller. Hydrogen plasma systems offer two distinct pathways for reducing metal oxides to metals. The first one is to apply *thermal plasma* in smelting reduction systems and the second one is to apply *non-thermal plasma* to effect reduction at the metal oxide-plasma interface. Thermal plasma refers to thermal equilibrium between all the species (i.e., free electrons, neutral species, ion, etc.) found in the plasma, which are characterized by high gas pressures ($p = 760$ torr or greater) and high gas temperatures (T = 3,000 K) as shown in Fig. 8. The term *cold* results from the fact that the temperature of the gas molecules in the plasma is significantly less than that of free electrons. This is due to a low collision rate in the low density gas (i.e., at low pressure). These plasmas are characterized by low pressure (typically, $p < 1$ atm) and low molecular temperature compared to equilibrium plasma [23–25]. As the pressure increases, the number of collisions between the particles also increases. Therefore, the amount of energy gained by the electrons between collisions decreases, and the cumulative amount of energy transferred from the electrons to the heavier particles such as neutral ions increases. As a result, the temperature of the electrons decreases, while the temperature of the heavier particles increases. As the pressure increases further, the collision frequency gives a uniform energy distribution among all plasma species. Here we summarize the research work carried out earlier based on available literature on reduction of oxide minerals by hydrogen plasma (Fig. 9).

Reduction of Iron Oxides Using Hydrogen

Industrially, iron is extracted from its ores—the major ores include hematite (Fe_2O_3) and magnetite (Fe_3O_4)—by carbothermic reduction in a blast furnace. The conventional industrial blast furnace process includes multiple stages and requires large-scale equipment. Iron oxides in the form of iron ore, either in lumpy form or as aggregates (sinter/pellet/briquette) are supplied to blast furnace for reduction. Coke is burned as a fuel to

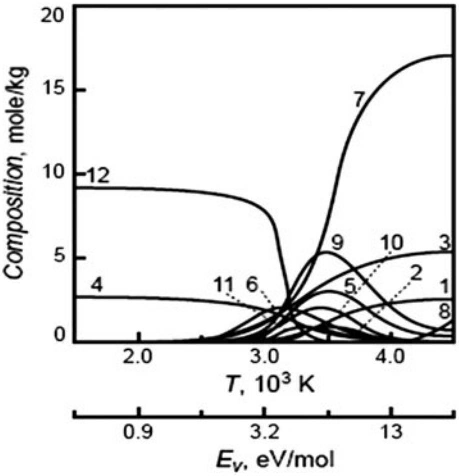

Fig. 9 Aluminum reduction from Al_2O_3 with molecular hydrogen in atmospheric-pressure thermal plasma. Composition of products: (1) O × 0.1; (2) O_2; (3) H × 0.1; (4) H_2 × 0.1; (5) OH; (6) H_2O; (7) Al; (8) Al+; (9) AlO; (10) Al_2O; (11) Al_2O_3 (condensed) [19]

generate gaseous products such as CO and CO_2 which reduce the metal oxides to produce iron at high temperature by the following reaction [19]:

$$Fe_2O_3 + 3CO \rightarrow 3CO_2 + 2Fe, \Delta H = -0.28 \text{ eV/mol} \quad (14)$$

Metallic iron produced in this way in the blast furnace contains carbon and is called pig-iron which requires de-carbonization to become steel. Reduction of iron oxides can be effected by hydrogen plasma. High plasma temperatures and the application of hydrogen intensify the process and help to avoid carbon in the product, which permits the whole steel manufacturing process to be accomplished directly and it leads to one-stage steel production [19, 26, 27].

The benefits of plasma reduction process for steel making arise from its ability to accommodate finely divided iron ore concentrates without pre-agglomeration which in turn allows greater degree of control of the plasma furnace compared to blast furnace. When successfully implemented on a large scale, plasma furnaces could potentially eliminate the need for coke ovens, agglomeration plants, blast furnaces, and oxygen steel making operations in future steel making technology [28]. The general reaction of reduction can be presented by the following reaction.

$$Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O \quad (15)$$

In thermal hydrogen plasma, H_2 gas is fed to the transferred arc plasma for its dissociation and ionization according to the applied electrical energy. The dissociated and ionised gases cool down at the arc-melt/solid oxide interface and partially combine again. This produces enormous amount of heat (enthalpy source) which supports the reduction of metal oxides that are typically endothermic in nature [5, 16]. The existence of dissociated H_2 is greatly dependant on the temperature at the interface. The rate of reduction has been found to be proportional to the amount of H_2 used. This means that the chemical reaction proceeds at a very high rate and the supply of H_2 is the rate limiting factor for reduction [29].

The interest in thermal plasma reduction of iron ore grew when Stokes [30] demonstrated the feasibility of one-stage production of pure iron by injection of iron oxide powder along with hydrogen directly into a helium plasma. Complete reduction was achieved by introducing Fe_2O_3 powder at a flow rate of 0.3 gm/min with hydrogen flowing at 13.6 lit/min into the helium plasma flame at corresponding power level of 15.5 kw. Subsequently, other researchers continued investigating the hydrogen reduction of iron ore in direct current plasma jet reactors [29, 31–38]. The plasma jet was operated with either pure hydrogen or a mixture of argon and hydrogen. Different size ranges of hematite concentrates were used. Also different systems were used to convey the ore into the plasma zone where the oxide particles were reduced in flight. These works demonstrated the feasibility of reducing iron oxide with hydrogen in a plasma reactor, though concerns over amount of energy needed and the mechanism of reduction reaction remained.

Gold et al. [32] and MacRae et al. [33] working at Bethleham steel corporation reported the development of a single-stage plasma reactor which directly converted iron oxide powders to molten iron using hydrogen and natural gas mixture. They noticed that the particles introduced tangentially to the plasma zone stick to the liquid dripping film at the surface of the anode. Further reduction and slagging were achieved at the bottom, in the liquid bath. Finally, the molten iron and slag were collected in a holding crucible, which was poured intermittently. The electrical energy consumption (5.41 eV/atom iron) nearly matched the theoretical value (4.58 eV/atom iron) by (1) controlling the gas composition (increase in the natural gas to hydrogen ratio), (2) using finer powder, and (3) scaling-up the reactor from 100 kW to 1 MW. Subsequently, in France, a direct iron-making method from iron ore by means of hydrogen plasma and natural gas has been tested on a l MW scale. However, the details are not available [36].

Dayal et al. [6] designed a plasma reactor known as the *rail reactor*, which produced a transient travelling arc. They reported in-flight reduction of 30 mg samples of MoO_3 and TiO_2 using hydrogen as reductant. Three factors were considered necessary for in-flight reduction to be successful: first, the availability of high energy atomic hydrogen throughout the reaction volume to enable the chemical reactions to proceed rapidly, second, retention of the oxide particles within the reducing atmosphere for sufficient time, and third, control of the background temperature well below 4,400 K which is the temperature that cause dissociation of water into hydrogen and oxygen. The rail reactor was conceived to satisfy these conditions. The reactor was designed in a manner that it produced an arc that entrained the gas in the reactor and produced atomic hydrogen in a relatively large volume that surrounded it as it moved. The atomic hydrogen produced by the arc existed for several milliseconds in the low temperature background after the arc had ceased to exist, suggesting that atomic hydrogen would remain for long enough duration in a practical size reactor. Metal oxides in powder and tablet form, reacted rapidly with the pulsed-arc treated atomic hydrogen compared to the rate of similar reactions using molecular hydrogen.

An important work of sufficient significance has been done under ULCOS programme where hydrogen plasma smelting reduction (HPSR) has been examined extensively at University of Leoben [9, 29]. Hiebler and Plaul [9] demonstrated the production of molten iron from its ore in a laboratory set up using hydrogen plasma. They named their process as the HPSR and their experimental results have led to the development of a concept for HPSR plant on industrial scale with the capacity to continuously produce an iron melt free of carbon and sulphur in a single stage using ore fines.

Badr et al. [29] examined the characteristics of the HPSR process, in terms of thermodynamics, kinetics, and scale-up potential. Their analysis covered the observations of previous workers [37–43]. One of the major observations is lower degree of hydrogen utilization when higher concentration of H_2 in H_2-Ar mixture was used. Hydrogen utilization improves when its concentration in the mixture is lower. Nakamura et al. [37] attributed this in part to the dissociated hydrogen present in the plasma. Moreover, they presumed that the separation of the oxide melt from the reduced iron might improve the reduction behavior, i.e., iron oxide alone would react with hydrogen. The other main observation is that the reduction potential of hydrogen increases almost two orders of magnitude just above the FeO melting point, with respect to that of the wustite phase. However, increasing the temperature up to the plasma temperature does improve the reduction rate but within the same order of magnitude. Further, the specific reduction rates of wustite and liquid iron oxide by H_2 and CO over a wide range of temperature were compared. It was observed that in the lower temperature range of 1,400–1,500 °C, H_2 reduction is approximately two orders of magnitude faster than that with CO. However, in the higher temperature range of 2,000–2,600 °C, this difference in kinetics by H_2 and CO diminishes and lies within the same order of magnitude. The H_2 plasma is approximately 3.4 times faster than the CO plasma. The activation energy for reduction by hydrogen plasma (23 kJ/mole) is less than one-sixth of the activation energy for reduction by CO plasma (150 kJ/mole).

Reduction of Oxides of Other Metals

Amongst all metals aluminium is second to iron with a global production of around 40 million tons per annum. It is extracted from bauxite by Bayer's process followed by fused-salt electro-winning in fluoride bath. Though this process is well developed, yet, involvement of carbon in anode making, fluoride emissions, and large production of red mud during alumina production are the most significant problems in aluminium production. Currently about 3.3 billion tons of red mud with dangerous properties of high pH value and strong alkalinity are accumulated in the world with an accumulation of over 120 million tons per year. The other categories of metals having extraction problems are the refractory metals. These metals belong to Groups IV B, V B and VI B of the periodic table. These metals require elevated processing temperatures due to their high melting points and associated Gibbs free energy of formation. In this context, the high temperatures and high gas enthalpies that can be achieved with plasma reactors are ideally suited for refractory metal production [44]. The plasma route for the production of refractory metals has good industrial prospect due to comparatively small scale of production and also due to non-availability of simpler technology. Plasma jet technology is rather prospective for reduction of oxides with low sublimation temperature which allows the substance to transfer into gaseous phase during its short residence in high temperature plasma zone. Hydrogen plasma intensifies the process as compared to Argon and Helium plasmas. High hydrogen conductivity increases the heat transfer from plasma to dispersed particles and low viscosity coupled with low density lead to longer acceleration time of particles and their residence time in high temperature zone [45].

The attention on extraction of refractory metals by hydrogen plasma grew when Stokes et al. [46] studied the reduction behaviour of WO_3, Fe_2O_3, Ta_2O_5, Al_2O_3, TiO_2 and ZrO_2 in an arc of helium plasma jet, as an extension of the work done by Groose et al. [47]. Using the plasma and 34 lit/min hydrogen flow into the plasma, they obtained maximum metal yields of 100 % for Fe_2O_3, 95 % for WO_3, and 25.6 % for Ta_2O_5. The respective powder flow rates were 0.3, 1.96, and 1.9 g/min respectively at corresponding power level of 15.5, 15.2 and 15.75 kW. Similar success was not achieved with Al_2O_3, TiO_2 and ZrO_2. However, the success achieved with WO_3, Fe_2O_3, and Ta_2O_5 demonstrates that the use of plasmas for reducing metallic oxides of refractory type is practically feasible. These oxides normally possess higher standard free energy and are easy to reduce. But the use of plasma would be much more justifiable if it could result in significant conversions for the oxides with lower standard free energy (less reducible) which lie in lower part of the Ellingham diagram, such as Al_2O_3, TiO_2 and ZrO_2. These three oxides, for which Stokes and associates [46] and also Kitamura et al. [39] obtained negligible metallization, have generally been considered to be much too stable to allow significant reduction.

In addition to reduction by atomic hydrogen, ionic hydrogen, or excited molecular hydrogen that are present in hydrogen plasma, *dissociative reduction* can also take place due to excessive high temperature associated with plasma. This opens up another pathway for extracting metals from their oxides (mainly refractory oxides). This is useful for metal oxides which have dissociation temperatures exceeding 4,500 K (e.g., refractory oxides) where oxygen and water are completely atomised [19]. Thermodynamic and kinetic analyses show that the high-temperature thermal plasma reduction processes follow the dissociative reduction mechanism [19, 48]. According to this mechanism, the reduction process starts with dissociation or atomization of the oxides with the formation of metal atoms and oxygen atoms. Then, during the quenching stage, oxygen atoms recombine with the available reducing agents, thereby restricting the reverse reactions giving rise to effective metal production. Interesting observations on dissociative reduction have been reported by Fridman [19] with respect to reduction of oxides. We discuss some of these points with respect to reduction of other metal oxides.

Tungsten

As mentioned earlier, Stokes et al. [46] obtained maximum metal yields of 95 % in case of WO_3 at powder flow rate 1.96 g/min and at corresponding power level of 15.2 kW. Tsvetkov et al. [49] using thermal arc discharges of hydrogen plasma jets with powers of 150 and 250 kW obtained up to 95 % yield. Ettingler et al. [50] used hydrogen in a helium plasma jet and Kim et al. [51] used in-flight plasma to reduce powders (20 μm) of $WO_{2.9}$ by H_2. They obtained metallization between 95 and 99.9 %. The reduction of tungsten oxide with hydrogen to produce metallic tungsten can be represented as.

$$WO_3 + 3H_2 \rightarrow W + 3H_2O \qquad (16)$$

The reaction proceeds through quasi-equilibrium composition of products after thermal dissociation of WO_3 at atmospheric pressure as shown in Fig. 10. The figure shows the composition of reaction products as a function of temperature. The highly energy intensive dissociation of tungsten oxide (WO_3) and formation of atomic tungsten (W) according to the following reaction takes place at very high temperature (about 5,000 K) where oxygen and water are completely dissociated to their respective atomic state.

$$WO_3 \rightarrow W + (3/2)O_2,\ \Delta H = 8.73\ \text{eV/mol} \qquad (17)$$

As mentioned earlier, water formation takes place only at the quenching stage due to recombination of free atomic oxygen with hydrogen which suggests that oxygen doesn't recombine with metal. An estimation of the energy cost of tungsten production from WO_3 in thermal plasma is shown in Fig. 11 for atmospheric pressure condition as a function of specific energy input for different quenching modes. The minimal energy cost in the absolute quenching mode corresponds to 35 eV per W atom, which can be achieved at a specific energy input of 30.5 eV/mol. Ideal quenching is assumed in this process where all intermediate tungsten oxides participate in recombination or disproportioning reactions during the fast cooling phase, forming atomic W and WO_3. The minimal energy cost of metal production in the case of ideal quenching corresponds to 30.6 eV per W atom. The super-ideal quenching in this process requires centrifugal separation of products. The

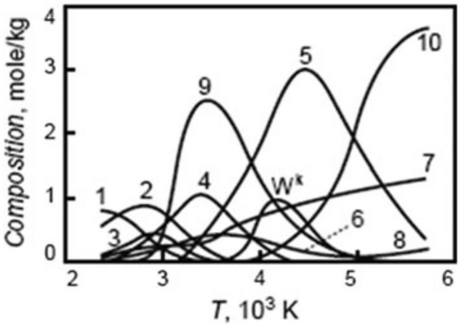

Fig. 10 Tungsten reduction from WO_3 by direct decomposition in atmospheric-pressure thermal plasma. Composition of products: (1)W_3O_9; (2)W_2O_6; (3)W_3O_8; (4)WO_3; (5)WO; (6) O_2; (7) O × 10; (8)W+; (9)WO_2; (10) W [19]

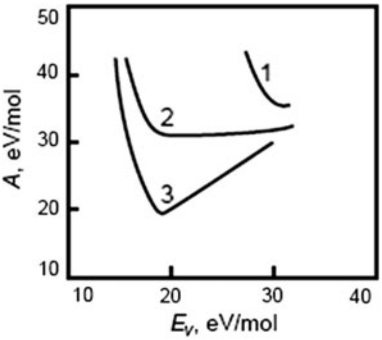

Fig. 11 Tungsten reduction from WO_3 by direct decomposition in atmospheric-pressure thermal plasma. Energy cost of tungsten production as function of specific energy input: (1) absolute quenching; (2) ideal quenching; (3) super-ideal quenching [19]

centrifugal effect permits one to decrease the energy cost to 19 eV per W atom level at a plasma temperature of 4,500 K [52]. However, It has been reported that W production by plasma route is cheaper than traditional routes because it consumes less energy and hydrogen gas (22 eV/atom and 2.6 Nm^3/kg) compared to traditional routes (40 eV/atom and 2.6 Nm^3/kg) [49] .

The process of reduction of tungsten oxide in hydrogen arc plasma using linear plasmatron (300 kW) and a direct-flow reactor has been developed on semi-industrial scale (INET, VNIITS, VNIIETO, USSR) [45]. By rapid cooling (quenching) metallic tungsten powder as globular particulates with a specific surface of 10–12 m^2/g was produced. After stabilizing the process parameters, relatively monodisperse powder in the size range of 40–50 nm was obtained. Also, by slow cooling (mild quenching), high purity tungsten powder (up to 0.02 % O_2) was obtained with particulate dimensions ($\sim$1 μm) close to commercial fine powders.

Molybdenum

Another example of reduction of refractory metal oxides by H_2 plasma is the reduction of molybdenum oxide (MoO_3) to produce metallic molybdenum (Mo) which can be represented as:

$$MoO_3 + 3H_2 \rightarrow Mo + 3H_2O \quad (18)$$

Effective production of Mo from MoO_3 by plasma route was experimentally demonstrated by Bolotov et al. [53]. The experiments were carried out in a high-temperature fluidized-bed reactor using hydrogen as a reduction agent and energy carrier. The hydrogen gas was heated up by an arc to a temperature level required for effective reduction of MoO_3. The characteristics of MoO_3 reduction are similar to those of WO_3. The quasi-equilibrium composition of the products of thermal MoO_3 dissociation at atmospheric pressure as a function of plasma temperature is shown in Fig. 12. The decomposition of MoO_3 into atomic molybdenum (Mo) and molecular oxygen takes place at very high temperature exceeding 4,500 K when oxygen and water are completely atomized:

$$MoO_3 \rightarrow Mo + (3/2)O_2 \quad \Delta H = 7.7\ \text{eV/mol} \tag{19}$$

As with tungsten, the energy cost of quenching of molybdenum has also been estimated. The minimal energy cost in the absolute quenching mode corresponds to 28 eV per Mo atom at a specific energy input of 25 eV/mol. This cost in case of ideal quenching corresponds to 25.4 eV per Mo atom and can be achieved at a specific energy input of 22.8 eV/mol. Super-ideal quenching with a centrifugal separation of the products lead to further reduction in the energy cost to 17.3 eV per Mo atom and can be achieved at a plasma temperature of 3,900 K [19]. Molybdenum production by plasma route is cheaper than that produced by traditional routes because it consumes less energy (29 eV/atom) and hydrogen gas (1.13 Nm^3/kg) compared to traditional routes; reduction by traditional routes consume 39 eV/atom of energy and 4.62 Nm^3/kg hydrogen gas [49].

Aluminum

Alumina (Al_2O_3) is a stable oxide which lies in the lower part of the Ellingham diagram. Hence it is a fairly stable oxide. Plasma reduction of Al_2O_3 has been tried by Fridman [19]. Figure 9 shows variations in the product composition with energy input for aluminium reduction from Al_2O_3 using molecular hydrogen in atmospheric pressure plasma. Alumina reduction takes place at temperatures of about 3,500 K. The minimal cost in absolute quenching mode is 29.4 eV per Al atom, which can be achieved at a specific energy input of 13.9 eV/mol with a degree of conversion of 94 % [19]. Unlike dissociative reduction mechanism of Tungsten and Molybdenum, disproportioning of AlO, AlO_2 and Al_2O during quenching gives rise to the formation of Al_2O_3 and Al [19]. It should be mentioned here that other metal oxides discussed below don't obey the dissociative reduction mechanism.

Titanium

Titanium is a strategic metal that can withstand harsh environmental attack. Due to its excellent fatigue and corrosion resistance, titanium alloys are used in aircraft, spacecraft,

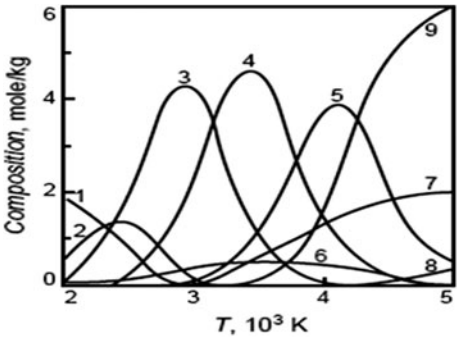

Fig. 12 Molybdenum reduction from MoO_3 by direct decomposition in atmospheric-pressure thermal plasma. Composition of products: (1) Mo_3O_9; (2) Mo_2O_6; (3) MoO_3; (4) MoO_2; (6) O_2; (7) O × 0.1; (8) Mo+; (9) Mo [19]

missiles, etc. As mentioned earlier, Stokes, et al. [46] could not reduce TiO_2. Kitamura et al. [39] also carried out in-flight reduction of TiO_2 powders in Ar-H_2 plasma and reported that TiO_2 vaporized as sub-oxides such as TiO. These are then precipitated as non-spherical particles and subsequently oxidized to stable oxides such as Ti_2O_3 and Ti_3O_5 during cooling. However, McLaughlin [54] patented a process of reduction of rutile (TiO_2) powders by hydrogen plasma. The process involves introduction of finely divided rutile into a plasma chamber where it melts into liquid droplets which is then contacted in counter current flow with hydrogen plasma. The purpose of hydrogen plasma was three-fold: (a) to heat TiO_2 to approximately 3,300 K, (b) to reduce the liquid titanium oxide to titanium and (c) to remove water and excess hydrogen from the reaction chamber in order to prevent reversal of the reaction upon cooling. The titanium metal is collected in liquid phase after treatment at 870 K in vacuum to remove excess hydrogen. Subsequently, McLaughlin [54] also utilised a Giannini P-140 plasma jet to reduce TiO_2 pigment (obtained from DuPont) packed into a hollow graphite cylinder with the plasma impinging normally at 3,100 K. At the end of the heating period, power was turned off, leaving the specimen to cool slowly in a bath of flowing helium gas, which contained Ti metal product with 99.8 % Ti, 0.1 % Al, and traces of Cu.

Chromium

Chromium is another strategic metal which is used in stainless steel and other special alloys. Huczko and Meubus [55] conducted the reduction of chromium oxide by introducing its vapour into Ar–H_2 RF plasma and obtained ultrafine metallic chromium powder. Kitamura et al. [39] also carried out in-flight reduction of Cr_2O_3 powders in Ar–H_2 plasma and obtained metallic Cr. They explained that the oxide particles in the plasma are heated quickly, and then those particles melt and eventually vaporize in metallic state. Finally, upon quenching, precipitation of non-spherical metal particles occurs.

Zirconium

Stokes et al. [46] studied the reduction of ZrO_2 in an arc of helium plasma jet and found no reduction of ZrO_2 in their chosen experimental conditions. Brown [56] also investigated reduction of ZrO_2 in Ar–C and Ar–H_2 arc plasma and found little advantage in the use of hydrogen as there was no reduction when either 250 or 150 μm particles of zirconia were charged. However, with 10 μm zirconia, a conversion of about 21 % was obtained.

Tantalum and Niobium

Tantalum and niobium are corrosion resistant metals and are obtained from two main ores: tantalite and pyrochlore. Stokes [57] could obtain about 50 % conversion of tantalum pentoxide (Ta_2O_5) into pure metallic tantalum using a helium plasma jet with addition of hydrogen. Shekhter et al. [58] have patented the method of preparing refractory metal by hydrogen plasma. Argon is added for plasma expansion since H_2 gives constricted plasma [18]. They carried out studies on particulates of Ta_2O_5 and Niobium oxides such as Nb_2O_5, NbO_2, and their mixtures. The temperature range of heated gas and the mass ratio of hydrogen gas to refractory metal oxides were found to be critical. Also, atomic hydrogen concentration in plasma was significant. Hence, to increase the rate of atomic hydrogen formation in the plasma, metal catalysts (Palladium, Platinum, Iridium, Ruthenium, Rhodium) in the form of particulates were used. In the temperature range of 1,900–2,900 K and mass ratio of H_2:Ta_2O_5 greater than 1.5:1, the metal yield was found to be 98 to 100 %. Furthermore, in case of Nb_2O_5, NbO_2 and their mixtures, in the temperature range of 2,100–2,700 K and a mass ratio of hydrogen gas to particulate greater than 9:1, 98 % yield was achieved.

Reduction of Oxides in Non-Thermal Plasma

Low Pressure

In recent years, several studies have been carried out to understand generation of plasmas and their properties from low to atmospheric pressure. Under low pressure cold plasma having low degree of ionization can be attained. Despite its inherent thermodynamic and kinetic advantages for reduction of metal oxides, only limited work has been performed. In the electronics industry it has been extensively used for the removal of surface oxides. Most of the work reported by in relation to electronics industry focuses on processing of group III-V semi conductors in radiofrequency plasmas. Cold plasma is used to remove the native oxide layers, which form naturally when semiconductor materials come in contact with air during fabrication of microelectronic circuits.

Removal of oxide layers from substrate is an important activity in electronic material processing which has been successfully carried out using plasma route [59–62]. Basically gallium-arsenide (GaAs) oxide layers on pure GaAs substrates and other native oxides on compound semiconductors are removed at gas pressures of around 10^{-4} torr and at moderate temperatures in the temperature range of 300–500 °C. Corresponding to these operating conditions, bombardment of molecular hydrogen is shown to have little effect on the oxide layer. Schade et al. [63] reported chemical reduction of various conductive transparent oxides such as tin oxide, indium-tin oxide, etc., in hydrogen plasmas using DC and RF discharge at 0.5 torr and 150–250 °C. Major et al. [64] reported the reduction of surface layers of indium-tin oxide and fluorine doped tin oxide films to yield elemental Indium and tin at 100 millitorr and 250 °C by RF plasma. Wallinga et al. [65] reported reduction of surface layers of fluorine based tin oxide by hydrogen treatment at 230 and 430 °C using RF decomposed hydrogen at 15 millitorr.

Brecelj et al. [66] showed 100 % reduction of copper oxide thin layers by hydrogen RF plasma at 7 millitorr and room temperature, whereas Sawada et al. [67] reported reduction of copper oxide thin films by hydrogen plasma generated by an atmospheric-pressure glow (APG) discharge. Baklanov et al. [68] reported cleaning of cupper surface by inductive plasma at 0.4 torr and optimal temperature of 200–350 °C. Ray et al. [69] patented the process for plasma treatment of metal oxide electrodes in electrochemical cells. They claimed reduction of 0.002–0.04 mm thick layer of metal oxides from the group consisting of silver oxide and cadmium oxide in RF plasma at 0.5 torr. Vesel et al. [70] obtained 100 % reduction of oxide layer in Fe–Ni alloys obtained from tokomaks plasma reactor by an inductively coupled RF generator at 0.5 torr. Michel et al. [71] reduced the surface oxides on steel up to 90 % by creating a plasma with dielectric barrier discharge (DBD). Aliev et al. [72] used a hydrogen plasma of electron cyclotron resonance (ECR) as the reducing medium to reduce films of higher vanadium oxide in the temperature range 295–625 K.

To date, the reduction of oxide materials in low pressure hydrogen plasmas does not appear to be an attractive industrial process. Flamm [73] suggests that the lack of interest in these plasmas is due to poor reaction rates and poor reproducibility of experimental data.

There are some reports by McTaggart [74] and Wertheimer et al. [75] claiming successful reduction of several oxides such as WO_3, FeO, Ta_2O_5, Al_2O_3, SiO_2, TiO_2, ZrO_2, HfO_2, ThO_2, CeO_2, MoO_3, Nb_2O_5, and V_2O_5 by hydrogen plasma at 1 torr pressure. Out of these oxides, complete reduction takes place for the first five oxides and other oxides transform to their respective lower oxides or protonated *golden oxides*.

Moderate Pressure

Moderate pressure plasma is nonequlibrium plasma, which is generated in the pressure range from 6 to around 100 torr. Though the temperature of molecular species of nonequlibrium plasma is significantly lower than those obtained in the equilibrium plasma, the electron temperatures are still large enough to produce substantial amount of chemically reactive species. These chemically reactive species stimulate the reaction at low to moderate temperatures [5, 23, 76, 77]. Hence, nonequilibrium plasma processing offers improved thermodynamics and kinetics over conventional thermal processing at reduced temperatures. Here we list some success stories and also discuss the difficulties associated with reduction of oxides using non-thermal plasma.

Reduction of Al_2O_3 powders in nonequilibrium plasma was attempted with the following operating conditions: pressure—10–100 torr; discharge current—5.10^{-2}–3 A; hydrogen flow rate—10^{-6}–10^{-4} nm^3/sec and temperature—3,000 K [78]. Altogether 60 % conversion of aluminum oxide with an energy consumption of 76 eV/mol of Al_2O_3 was obtained. Later, Lyubochko et al. [79] noted four main problems encountered in a quasi-equilibrium plasma for Al_2O_3: (1) the difficulty of introducing a substance into a high temperature discharge zone, (2) insufficient duration of stay in this zone (10^{-3}–10^{-1} s), (3) the release of reaction products and inhibition of reverse reactions, and (4) the yield of product amounting to only 30 % with associated contamination of product by lower oxides. Bullard and Lynch [23] used a microwave generator at 2.45 GHz (6–30 torr, 888–1,241 K, 0.4–1.2 kW) to study the reduction of ilmenite ($FeO.TiO_2$) powders. The sample holder was continuously rotated at 15 rpm while in contact with plasma to guarantee uniform temperature distribution. The results indicated that the reduction by hydrogen plasma was as much as 420 % higher than that predicted for conventional reduction with molecular hydrogen. Despite its demand, only a few studies have been reported on reduction of titanium oxide by hydrogen plasma [4, 21, 23]. Zhang et al. [21] reduced tablets (11 mm diameter, 2 mm thickness) of TiO_2 to Ti_2O_3 with cold hydrogen plasma generated by a DC pulsed glow discharge at 19 torr, 960 °C, and 60 min of operational time. While using molecular hydrogen very little amount of $Ti_{10}O_{19}$ and Ti_9O_7 species were detected and the dominant oxide was unreduced TiO_2. The enhancement of reduction in plasma is thought to be an effect of active hydrogen species and oxide reduction with these hydrogen species needs smaller activation energy.

Reductions of iron oxides by non-thermal plasma have been tried. Zhang et al. [16] obtained reduction of tablets of Fe_2O_3 to metallic iron with cold hydrogen plasma (11 torr and 490 °C) which was not possible with molecular hydrogen. The reaction path was found to be $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe$. The polarity was found to have a critical role. They reduced Fe_2O_3 in cold plasma by making the sample (1) anode, (2) neutral and (3) cathode. There was no indication of reduction when the sample was made anode. Only a little reduction occurred when the sample was made neutral. However, when the sample was made cathode, the reduction increased substantially. Rajput et al. [7] obtained nearly complete reduction of powder tablets (40 mm diameter, 3 mm thick) of Fe_2O_3 by hydrogen plasma in a 2.45 GHz microwave generator at 40 torr and 573 K. The reduction followed a sequential path: $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$. At the working temperature (573 K), reduction by molecular hydrogen was insignificant. Based on the experimental results and available data from literature [19, 22, 80], Rajput et al. [7] concluded that reduction of haematite at low temperature in hydrogen plasma is probably occurring due to vibrationally excited hydrogen molecules.

Summary

Plasma processing of metal oxides is an interdisciplinary field which requires knowledge of both plasma physics and metallurgical engineering. The selected literature discussed here elucidates various aspects of reduction of oxides by hydrogen plasma. It is established that hydrogen plasma provides thermodynamic advantages for reduction of oxides because of the presence of atomic, ionic, as well as excited hydrogen species that are energetically much more effective in reducing metal oxides compared to molecular hydrogen. Furthermore, the kinetic barrier associated with hydrogen plasma reduction processes can be removed because of higher local temperatures generated due to plasma assisted reactions. Typically the activation energy of the plasma assisted reactions is lower compared to the corresponding standalone reactions. It is shown that both thermal plasma as well as non-thermal cold plasma can be effectively used for the reduction purpose. Oxide dissociation and dissociative reduction can also be effectively used due to generation of very high local temperatures during plasma operation. Overall, hydrogen plasma processing to reduce oxide minerals provides a potential future option.

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