https://doi.org/10.26160/2474-5901-2026-52-32-40

THERMODYNAMIC AND TECHNOLOGICAL JUSTIFICATION FOR THE USE OF HYDROGEN IN THE REDUCTION OF OXIDES OF STRATEGICALLY IMPORTANT METALS

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Keywords: hydrogen reduction, strategically important metals, oxide chemistry, thermodynamics of reduction, Gibbs free energy, gas phase.
Abstract. The article considers the problem of using hydrogen as a reducing agent in the processing of oxides of strategically important metals under the transition of the metallurgical industry to low-carbon technologies. The influence of the oxide chemistry features of nickel, cobalt, vanadium, and rare earth elements on the thermodynamic feasibility of hydrogen reduction processes is analyzed. The role of the main thermodynamic parameters, including the Gibbs free energy change, the temperature factor, and the composition of the gas phase, as well as their influence on the extent and direction of reduction reactions, is studied. Special attention is paid to the technological aspects of implementing hydrogen reduction, such as the choice of reactor type, mass transfer and kinetic limitations, and control of the partial pressure of hydrogen and water vapor.

ТЕРМОДИНАМИЧЕСКОЕ И ТЕХНОЛОГИЧЕСКОЕ ОБОСНОВАНИЕ ИСПОЛЬЗОВАНИЯ ВОДОРОДА В ВОССТАНОВЛЕНИИ ОКСИДОВ СТРАТЕГИЧЕСКИХ МЕТАЛЛОВ

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Ключевые слова: водородное восстановление, стратегически важные металлы, оксидная химия, термодинамика восстановления, энергия Гиббса, газовая среда.
Аннотация. В статье рассматривается проблема применения водорода в качестве восстановителя при переработке оксидов стратегически важных металлов в условиях перехода металлургической отрасли к низкоуглеродным технологиям. Анализируется влияние особенностей оксидной химии никеля, кобальта, ванадия и редкоземельных элементов на термодинамическую реализуемость процессов водородного восстановления. Исследуется роль основных термодинамических параметров, включая изменение энергии Гиббса, температурный фактор и состав газовой среды, а также их влияние на глубину и направленность восстановительных реакций. Отдельное внимание уделено технологическим аспектам реализации водородного восстановления, таким как выбор типа реакторов, массообменные и кинетические ограничения, управление парциальным давлением водорода и водяного пара.

Introduction

The process of reducing oxides of strategically important metals is an essential step in creating high-tech value chains that provide the foundation for the development of the energy sector, electronics industry, mechanical engineering, battery production and energy storage systems. Metals such as nickel, cobalt, vanadium, and rare earth elements (REE) are backbone elements in industries that have high demands on the efficiency, environmental friendliness, and sustainability

of the technologies used for their production and processing. Traditional metallurgical processes for the reduction of metal oxides mainly depend on the use of carbon-based reducing agents, which is associated with high costs for emissions of CO_2 and other oxidizing gases.

Under the conditions of the global energy transition, the tightening of environmental regulations, and the development of mechanisms for regulating greenhouse gas emissions, there is an increasing need to develop and implement alternative reduction technologies with a lower carbon footprint. One of the most promising directions in this context is the use of hydrogen as a reducing (HR) agent in metallurgical processes. In this case, the oxidation product is water vapor, which fundamentally changes the environmental profile of the processes and opens possibilities for more flexible control of the gas atmosphere. The objective of this research is to provide a thermodynamic and technological justification for the feasibility of using HR of oxides of strategically important metals.

Main part. Strategic metals and features of their oxide chemistry

Strategic metals form a special group of elements that are essential for the functioning and development of modern high-technology industries. Their significance is determined by a combination of unique physicochemical properties and limited availability, which makes the technologies for the production and processing of these metals a subject of increased scientific and industrial interest (fig. 1).

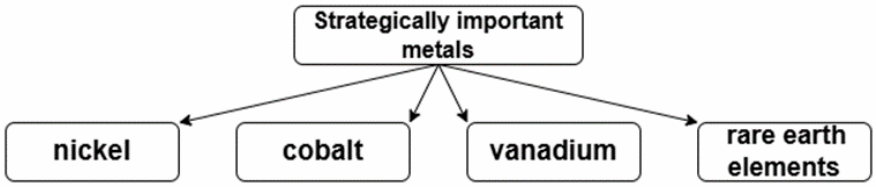

Fig. 1. Main groups of strategically important metals

Nickel and cobalt are the main components of rechargeable batteries, heat-resistant and corrosion-resistant alloys, and catalysts that determine the performance characteristics of materials in the energy sector and the chemical industry. Their basic oxides have a stable crystalline structure and, as a rule, are reduced to a metallic state in one stage. This makes these processes relatively predictable from a thermodynamic point of view and less sensitive to changes in technological parameters.

Vanadium occupies an intermediate position in terms of the complexity of reduction processes. It is widely used in steel alloying, increasing strength and wear resistance, and is also used in electrochemical energy storage systems. A distinctive feature is its pronounced multivalency, which leads to the existence of several stable oxide forms. The reduction of vanadium oxides is sequential and proceeds through a series of intermediate stages, which significantly complicates both thermodynamic analysis and practical implementation.

The oxide chemistry of **REE** is the most complex. These metals play an important role in the production of magnetic materials, electronic components,

optoelectronic devices, and catalysts, however, their oxides are characterized by high thermodynamic stability. The high metal–oxygen bond energy and features of the electronic structure lead to the persistence of oxide phases over a wide range of temperatures (T) and oxidation potentials. As a result, direct reduction is thermodynamically difficult and, as a rule, requires either extreme conditions or the use of multistage and combined technological routes [1].

Thus, differences in oxide chemistry determine the nature and complexity of reduction processes. These features form thermodynamic and technological prerequisites that must be taken into account when analyzing the possibilities of using HR.

Thermodynamic patterns and conditions for HR of oxides of strategically important metals

An important thermodynamic parameter characterizing the course of the reduction reaction is the **standard Gibbs free energy change** ($\Delta G°$). It makes it possible to assess the thermodynamic feasibility of the process under standard conditions and is determined by the following relationship:

$$\Delta G° = \Delta H° - T\Delta S°, \quad (1)$$

where $\Delta G°$ – standard Gibbs free energy change of the reaction; $\Delta H°$ – standard enthalpy change of the reaction; $\Delta S°$ – standard entropy change; T – absolute temperature of the system, expressed in kelvin.

Negative values of $\Delta G°$ indicate the thermodynamic feasibility of the reduction process, whereas positive values indicate the stability of the oxide phase under the given conditions [2]. **The dependence of this parameter on** T plays a crucial role, since its increase reduces the thermodynamic stability of oxides due to an increase in the entropy contribution.

The composition of the gas phase also has a significant influence on the equilibrium of reduction reactions. An increase in the partial pressure of hydrogen or a decrease in the water vapor content shifts the equilibrium toward the formation of the metallic phase, whereas an increase in the fraction of water vapor contributes to oxide stabilization and may lead to reverse oxidation of the metal. Thus, control of the gas-phase composition is an integral tool for ensuring the thermodynamic feasibility of HR. Even in cases where $\Delta G°$ is close to zero, a decrease in the partial pressure of water vapor through its removal from the reaction zone makes it possible to shift the equilibrium toward the metal, which is of fundamental importance for the reduction of thermodynamically stable oxides.

These patterns manifest differently for individual groups of strategic metals. For **nickel and cobalt oxides**, HR is characterized by relatively favorable conditions. In these systems, pronounced multistage behavior is generally absent, and the transition to the metallic state can proceed directly in accordance with the reaction:

$$MeO + H_2 \rightarrow Me + H_2 0 \quad (2)$$

where MeO – nickel or cobalt oxide; Me – metal in the reduced state;

H_2 – molecular hydrogen acting as the reducing agent; H_20 – water vapor formed as a result of the reduction.

Within the technologically acceptable T range, the reduction remains thermodynamically favorable, which makes it possible to achieve a high degree of conversion without the need for extreme heating. The depth of reduction in these systems is largely determined by the ratio of the partial pressures of hydrogen and water vapor, which is included in the expression for the isobaric potential of the reaction:

$$\Delta G = \Delta G^\circ + RT \ln \frac{pH_2 0}{pH_2}, \quad (3)$$

where ΔG – Gibbs free energy change of the reaction under real conditions; ΔG° – standard Gibbs free energy change of the reaction; R – universal gas constant; T – absolute temperature; pH_2 and pH_20 – partial pressures of hydrogen and water vapor, respectively.

For **vanadium oxides**, the thermodynamic picture becomes significantly more complex due to the pronounced multivalency of the metal. The reduction proceeds sequentially through a series of intermediate oxide phases with lower oxidation states, which can be represented by the following scheme:

$$V_2O_5 \rightarrow V_2O_3 \rightarrow VO \rightarrow V, \quad (4)$$

where V_2O_5, V_2O_3, and VO – vanadium oxide phases with different oxidation states; V – metallic vanadium. Each reduction stage is characterized by its own ΔG°, and the temperature dependence reflects differences in the thermodynamic stability of the intermediate phases.

The transition from highly oxidized forms to less oxidized ones can be thermodynamically favorable even at moderate T, however, more stringent conditions are required to obtain metallic vanadium. In these systems, the composition of the gas phase becomes critically important, since even a slight increase in the fraction of water vapor can stabilize oxide phases and limit the depth of reduction.

Oxides of REE are characterized by even higher thermodynamic stability. This is due to the significant metal–oxygen bonding energy and the peculiarities of their electronic structure. Over a wide T range, they remain stable; as a result, their direct HR under moderate conditions is thermodynamically hindered. The implementation of this mechanism in such systems is possible either at high T, or within the framework of combined and multi-stage technological routes.

For a generalized interpretation of the described patterns, it is appropriate to use Ellingham diagrams, which represent $\Delta G^\circ(T)$ for oxidation reactions. As a reference, the following reaction is used:

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2 0, \quad (5)$$

where H_2 – molecular hydrogen; O_2 – molecular oxygen; H_20 – water vapor formed as a result of hydrogen oxidation.

The $\Delta G°(T)$ ependence serves as a thermodynamic guideline when compared with the oxide formation lines of metals on Ellingham diagrams. The intersection of the curves corresponding to the hydrogen oxidation reaction and the metal oxide formation reactions allows us to determine the ranges of T values in which the condition $\Delta G° < 0$ is fulfilled, which indicates the thermodynamic feasibility of the reduction processes. On this basis, the regions of preferential application of hydrogen and carbon reduction routes are identified, and the boundary between oxidizing and reducing regimes of the gas phase is determined.

Technological aspects of HR

The practical implementation of HR of oxides of strategic metals is determined not only by the thermodynamic feasibility of the processes, but also by a set of technological factors that affect reaction kinetics, mass transfer efficiency, and the operational stability of the equipment.

In industrial and pilot-scale practice, various types of reactors are used for HR, differing in design and in the modes of interaction between the gas and solid phases. The most common include tubular and chamber furnaces, shaft units, and fluidized-bed reactors, a comparative characterization of which is presented in table 1.

Tab. 1. Comparative characteristics of the main types of reactors [3, 4]

Reactor type	Main advantages	Main limitations
Furnace reactors	The relative simplicity of the design, high flexibility of T control, ease of use in laboratory and low-tonnage processes, efficiency in the restoration of relatively simple oxide systems.	Uneven T field, difficult removal of water vapor from the reaction zone, limited intensity of mass transfer.
Mine reactors	Stable countercurrent contact of solid and gas phases, more efficient use of hydrogen, simplified control of the composition of the gas medium.	The need for careful optimization of hydrodynamic conditions, the risk of channeling the gas flow, increased requirements for uniformity of loading.
Fluidized bed reactors	Intensive mass and heat exchange, uniform T distribution, high speed of recovery processes.	Increased requirements for the granulometric composition of raw materials, abrasion and degradation of particles, complication of hardware design.

Regardless of the reactor type, the efficiency of HR is largely determined by **mass transfer and kinetic limitations**. The reduction process includes successive stages of hydrogen diffusion to the surface of the oxide particle, chemical interaction at the phase boundary, and removal of water vapor from the reaction zone. When dense metallic or suboxide layers form on the particle surface, diffusion inhibition may occur, slowing further reduction. This effect is especially

pronounced for thermodynamically stable oxides and multivalent systems, in which the formation of intermediate phases leads to a more complex kinetic picture of the process [5].

From a quantitative perspective, the influence of kinetic factors on the rate of HR can be described through the T dependence of the reaction rate constant. In the first approximation, it follows the Arrhenius relationship:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right), \quad (6)$$

where k – the rate constant of the reduction reaction; k_0 – pre-exponential factor characterizing the frequency of effective collisions of reacting particles; E_a – activation energy of the reduction process; R – universal gas constant; T – absolute temperature.

This relationship makes it possible to explain the acceleration of recovery processes with increasing T values, as well as differences in reduction kinetics for oxides with different structures and metal–oxygen bond energies. Under conditions where dense metallic or suboxide layers form on the particle surface, the kinetic regime may shift from chemically controlled to diffusion limited.

A significant technological factor is **control of the gas atmosphere composition**, primarily the ratio of hydrogen to water vapor. As shown in the thermodynamic analysis, the accumulation of water vapor shifts the equilibrium toward the oxide phase and can limit the extent of reduction even under favorable T conditions. In practical schemes, this effect is compensated by the organization of a flow regime, the use of counterflow of gas and solid phases, and the use of water vapor removal and condensation systems in the cold sections of the installation. Maintaining a low partial pressure of water vapor in the reaction zone is an important condition for implementing HR of thermodynamically stable oxides.

Additional factors affecting the efficiency of the process include the **overall system pressure and recovery mode**. An increase in the hydrogen potential of the gaseous medium at a given mixture composition contributes to a shift in equilibrium towards the metallic phase and intensifies the kinetics of reduction reactions. At the same time, operation at high pressure places significant demands on the tightness of the equipment and the safety of operation. The modes also have different effects on the efficiency of the process. Continuous circuits provide more stable conditions and high productivity, while periodic modes provide greater flexibility and are suitable for processing complex or variable materials.

Overall, the analysis of the technological aspects of HR shows that achieving a high degree of conversion of oxides of strategic metals is possible only with coordinated optimization of the thermodynamic and technological parameters of the process. A rational choice of reactor type, control of mass transfer and gas atmosphere composition, and proper adjustment of pressure and reaction mode make it possible to realize the potential of hydrogen schemes and ensure their competitiveness compared with traditional carbon routes.

Comparative analysis of methods for reducing oxides of strategically important metals

Comparison of hydrogen and carbon technological routes for the reduction of oxides of strategically important metals requires a comprehensive analysis. Despite the common objective, these approaches fundamentally differ in the reduction mechanism, the nature of thermal regimes, and the consequences for subsequent stages of metallurgical processing (tab. 2).

Tab. 2. Comparative characteristics of hydrogen and carbon routes for the reduction of oxides of strategically important metals [6, 7]

Comparison criteria	Hydrogen routes	Carbon routes
Reducing agent and gas environment	Hydrogen, the reaction of hydrogen and oxygen, resulting in the formation of water with the possibility of flexible regulation of the reduction potential.	Carbon and carbon monoxide, reaction of carbon with carbon dioxide to form carbon monoxide and limited controllability.
Energy and *T* regime	The ability of a number of oxides to operate at moderately high *T*, potentially lower specific energy consumption when optimizing the composition of the gas medium.	Processes with high *T*, increased energy consumption and heat loss.
Environmental profile	The main product of the reaction is water vapor, low direct carbon dioxide emissions when using low-carbon hydrogen.	Significant emissions of carbon dioxide and related gases, high carbon footprint.
Metal product quality	Minimal carburization, absence of carbide phases, simplification of subsequent refining stages.	Possible formation of carbides and carburization, complication of purification and processing.
Regulatory factors	Compliance with decarbonization strategies and environmental requirements.	Increased regulatory and economic risks with stricter environmental regulations.

Thus, the comparison shows that hydrogen-based schemes have significant potential in terms of environmental efficiency and product quality. However, their practical implementation is associated with a number of thermodynamic and technological limitations.

An important factor is the **high thermodynamic stability of oxides of certain metals**, for which HR is possible only within a narrow *T* range and under strictly controlled gas atmosphere composition. In such systems, even a slight increase in the partial pressure of water vapor can shift the equilibrium toward the oxide phase and significantly reduce the extent of reduction. This requires the use of intensive measures to control the gas atmosphere and remove reaction products.

Technological risks of HR are associated both with kinetic limitations and with the specific features of process equipment design. The formation of dense

metallic or suboxide layers on the surface of particles can lead to diffusion inhibition and a slowdown of reduction, especially when processing thermodynamically stable and multivalent oxide systems. Additional problems arise due to the requirements for tightness of equipment, safety when handling hydrogen, and the resistance of structural materials to high T and a reducing atmosphere. These factors limit the scalability of certain technological solutions and increase the requirements for engineering development of the processes. For a number of strategically important metals, HR within single-stage schemes is insufficient, which **necessitates the use of combined and multistage routes**.

A promising area of development is the **integration of hydrogen technologies with alternative reduction and metallothermal processes**, including the use of aluminum, magnesium or calcium as reducing agents at other stages. Such hybrid schemes make it possible to combine the environmental advantages of hydrogen with the high reducing capability of metallothermic reactions, ensuring deeper reduction of thermodynamically stable oxides. Additional opportunities arise when **HR is integrated with the processes of preliminary chemical modification of the feedstock, aimed at reducing the stability of the oxide phases**.

Further research should focus on deeper thermodynamic and kinetic analysis of specific oxide systems, the development of effective methods for controlling gas atmosphere composition, and the optimization of reactor designs. Studies aimed at scaling processes from laboratory and pilot levels to industrial units, as well as evaluating the integration of hydrogen technologies into existing metallurgical chains, are of significant importance. Overall, the development of these directions will make it possible not only to increase the technological feasibility of HR, but also to determine its role in the long-term transformation of the metallurgical industry under decarbonization conditions [8].

Conclusion

The modern transformation of the metallurgical industry is increasingly driven by the need to identify technological solutions that combine efficient processing of mineral raw materials with the requirements of environmental sustainability and resource rationality. In this context, HR of oxides of strategically important metals represents one of the most promising directions in the development of metallurgical processes, capable of changing traditional approaches to the production of metallic materials. Thermodynamic and technological analysis shows that the use of hydrogen has a solid scientific basis and can be implemented provided that optimal T regimes, gas atmosphere composition, and reactor system design solutions are maintained. At the same time, the complexity of the oxide chemistry of certain metals necessitates a differentiated approach and, in some cases, the use of multistage and combined technological routes.

From a practical perspective, the potential implementation of HR technologies in the metallurgical industry can ensure a significant reduction in the carbon footprint of production and increase the environmental sustainability of the

industry as a whole. At the same time, the transition to hydrogen-based schemes may contribute to the growth of the competitiveness of metallurgy by improving product quality, reducing regulatory risks, and integrating into the emerging low-carbon industrial ecosystem.

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Received 06.02.2026