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Study of the Ion Dissociation Process during the Reduction of Metal Oxides

Abstract: In the present work, an attempt was made to experimentally confirm the possibility of ion dissociation of a metal oxide as one of the stages of the reduction process. Additionally, a solid, nonvolatile reducing agent was employed to investigate the feasibility of a dissociative reduction mechanism. A common feature of all the experiments was the use of a non-contact reduction technique. This experimental approach makes it possible to investigate individual processes occurring on the surfaces of the reductant and the oxide. An essential requirement in this case is the use of low-volatility oxides and reducing agents.

Keywords: ion dissociation; reduction of metal oxides; iron oxide; copper oxide; gas-phase ionization.

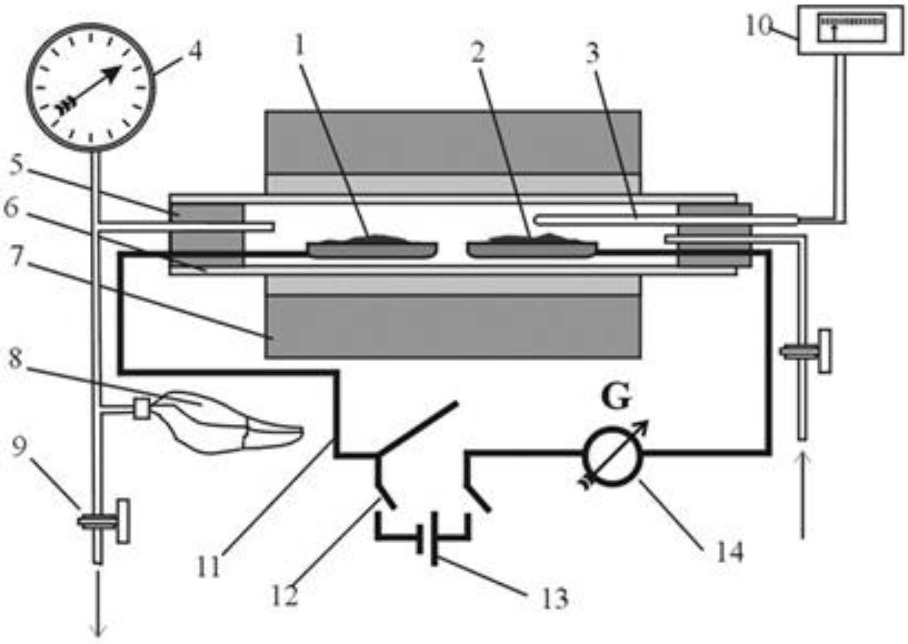
Introduction

The reduction of metal oxides plays a key role in metallurgy, solid-state chemistry, and functional materials technology. Despite the extensive study of the thermodynamic and kinetic aspects of these processes, their atomic-level mechanisms often remain the subject of scientific debate (El-Geassy et al., 2013; Yuan et al., 2021). One possible reduction pathway involves ion dissociation of oxides, leading to the formation of charged species that participate in oxygen transfer between the oxide and the reducing agent. However, experimental verification of this mechanism is challenging due to the difficulty of isolating and detecting ion fluxes generated directly within the reaction zone (Geld, 1957; Zhang et al., 2016).

In recent years, non-contact research methods have attracted increasing attention, as they eliminate the influence of electrical connections and external charge carriers on experimental outcomes (Hammam et al., 2022). These methods create conditions under which the recorded electrical signals can be directly correlated with the reduction process itself, including potential oxygen ionization during oxide lattice dissociation. An important feature of such experiments is the requirement to use low-volatility oxides and reducing agents, which prevents masking effects associated with gas-phase reaction products (Kenzhaliyev et al., 2022).

Research methods

A special experimental setup (Figure 1) was designed to investigate the possibility of ion dissociation of iron and copper oxides.



1 – oxide sample; 2 – reductant sample; 3 – thermocouple; 4 – manometer; 5 – stoppers; 6 – alumina tube; 7 – heating furnace; 8 – expansion vessel; 9 – valve; 10 – recording device; 11–14 – elements of the external electric circuit

Figure 1. Set up for recording ion currents during the reduction of oxides using a non-contact method

The setup consisted of an alumina tube, sealed at both ends with rubber stoppers, placed in a furnace heated up to 1200 °C. Inside the tube, within the heating zone, two iron crucibles were positioned 5 mm apart. Each crucible was connected to an iron electrode passing through a rubber stopper to the outside of the alumina tube. The pressure and composition of the gas phase could be adjusted via tubes embedded in the rubber stoppers. The temperature inside the tube was measured using a platinum thermocouple. One of the crucibles contained iron oxide, while the other contained metallic titanium in the form of shavings. The ends of the iron electrodes were connected by a copper wire to a potentiometer. In some experiments, a direct current (DC) power source was included in the resulting electrical circuit. A vacuum could be created inside the tube using a vacuum pump after preliminary purging with an inert gas (argon).

Before the main experiments, “blank” tests were conducted on the setup. The interior of the alumina tube was filled with argon, and no samples were placed in the iron crucibles. The furnace was heated to the experimental temperature of 1200 °C. No current or voltage was detected in the external electrical circuit. Similar tests were carried out after evacuating the alumina tube, and again, no readings were observed on the potentiometer.

Subsequently, a series of experiments was performed with identical iron oxide samples in both crucibles. Similar experiments were conducted with titanium and titanium dioxide samples. In these cases, no potentiometer readings were observed either. All series of blank experiments described above were repeated with a 50 V DC power source connected to the external circuit. Under these conditions, an electric current became noticeable in the system at a temperature of 600 °C under atmospheric argon pressure, reaching 2-4 µA. As the temperature increased to 1000 °C, the current gradually rose to 2 mA. When the system was evacuated to a pressure of 10^3 Pa, the current decreased by roughly a factor of ten, but still increased with rising temperature. The magnitude of the current was the same for both direct and reverse connections of the DC power source.

Results and discussions

The preliminary experiments demonstrated that in the electrical system without samples or with identical samples under the conditions described above, no electromotive force (voltage) or current was observed between the iron electrodes. It was determined that at temperatures of 600 °C and above, the gas phase inside the alumina tube becomes sufficiently ionized to conduct an electric current with the parameters described earlier.

The main series of experiments was conducted with iron oxide in one crucible and titanium shavings in the other, the latter taken in a tenfold excess relative to the amount required for complete oxidation of the iron oxide. Under these conditions, at temperatures above 500 °C, a voltage of 0.2-1.0 mV appeared in the external circuit. No current was recorded. During a 15-minute hold at this temperature, no changes in the electrical parameters were observed. Changes in the system pressure, whether increased or decreased, caused the voltage to drop to zero; however, 1.5-2.0 minutes after stabilization of the pressure, the voltage gradually returned to the value it had prior to the pressure change.

Further temperature increase led to a rise in both voltage and current. The maximum voltage of 35 mV and current of 40 μA were obtained at 1200 °C, both under vacuum and at atmospheric pressure. It should be noted that the electrical parameters, especially at temperatures between 500-700 °C, were unstable. However, there was a general trend of increasing current between the iron oxide and titanium samples with rising temperature (Figure 2). At temperatures of 700 °C and above, the iron oxide sample acted as the positive pole, while the titanium sample acted as the negative pole.

Reversed polarity was observed in some experiments during sharp pressure fluctuations in the gas phase at temperatures below 700 °C. At higher temperatures, changes in pressure caused a significant drop in voltage, followed by a gradual recovery to a value close to that before the pressure change. The time required for the voltage to return to its original value varied between 5 minutes (at 1100-1200 °C) and 20 minutes (Figure 3).

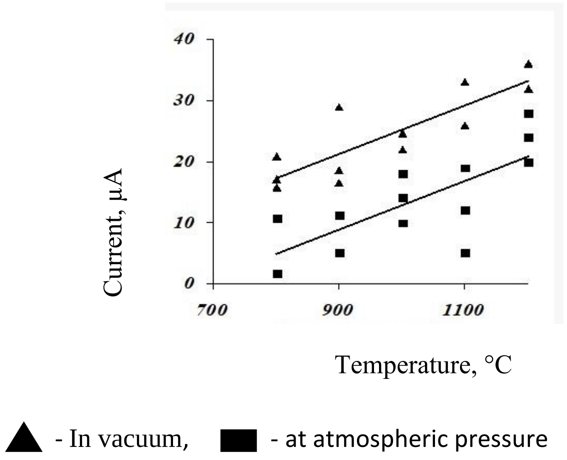


Figure 2. Variation of the current between the iron oxide and the reductant samples as a function of temperature

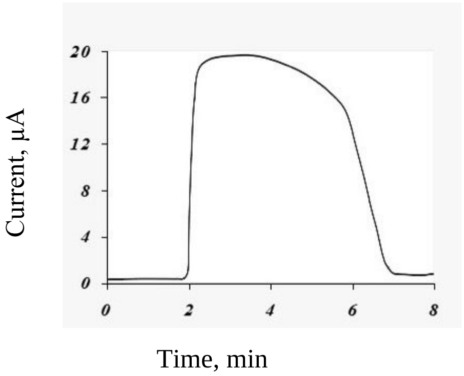


Figure 3. Variation of the current between the oxide and the reductant over time

It should be emphasized that voltage and current decreased with both increasing and decreasing pressure. The magnitude of the change in current and voltage with pressure varied across experiments and sometimes dropped to zero.

Clearly, the emf between the samples only occurs when the processes of iron oxide reduction by titanium occur simultaneously and ceases when the iron oxide is completely reduced to metal.

Similar experiments were conducted with cuprous oxide. However, due to the relatively high rate of cuprous oxide reduction, the process was completed within a few minutes (3-5), and stable electrical parameters were not recorded. The current varied from 1 to 28 microamps, and the voltage from 1-2 to 30 millivolts.

A series of experiments was subsequently conducted with a DC power source connected to the electrical circuit. The connection was made in two ways: in the first, the negative pole was connected to a sample of iron oxide, and the positive pole to titanium filings (direct connection); in the second, the opposite was true (reverse connection).

The iron oxide-titanium system in this case represented a source of direct current emf, connected to the overall electrical circuit.

In all these experiments, the rate of iron oxide reduction was virtually identical to the rate previously recorded in experiments without a direct current source.

The experiments conducted allow us to conclude that during the reduction of copper oxide by metallic titanium, a potential difference arises between the oxide and the titanium. Assuming that the partial pressure of negatively charged oxygen ions above the oxide is proportional to the equilibrium partial pressure of oxygen above it, the occurrence of this potential difference can be explained as follows. In this case, the partial pressure of ionized oxygen above iron oxide should be greater than that above the titanium dioxide coating the titanium surface. When iron and titanium oxide samples are combined, the positive charge on the iron oxide sample is greater because it releases a greater number of negatively charged oxygen ions into the gas phase. Thus, a potential difference arises between the iron and titanium oxide samples, with iron oxide having a positive charge and titanium having a negative charge. This potential difference was recorded in the experiments described above. When an external electrical circuit is closed, an electric current is observed, disrupting the equilibrium in the iron oxide-titanium-oxygen ion gas-phase system. The system attempts to restore equilibrium by further releasing oxygen ions from the iron oxide and reacting with titanium. Thus, in the external electrical circuit, charge transfer from titanium to iron oxide is accomplished by electrons, while in the internal circuit, charge transfer from iron oxide to titanium is accomplished by negatively charged oxygen ions. The current in this system is too low for the mass transfer of ionized oxygen to make a significant contribution to the overall rate of iron oxide reduction.

The conducted studies experimentally confirmed the possibility of ionic dissociation of iron oxide with the release of negatively charged oxygen ions into the gas phase during its reduction with metallic titanium using a contactless method. During the reduction of iron oxide with metallic titanium, conditions were created for an electrochemical reduction mechanism through the exchange of oxygen ions and electrons between the oxide and the reducing agent. However, due to its poor mass transfer characteristics, this mechanism cannot significantly contribute to the overall rate of iron oxide reduction.

Thus, most of the views expressed in the literature on the mechanism of metal oxide reduction are not at all contradictory. They all describe a single process of metal oxide reduction, the mechanism of which significantly depends on the combined influence of many different factors, many of which can already be listed. These include the physicochemical properties of the oxides being reduced, the reducing agents used, and their reaction products, temperature, gas phase pressure, oxygen partial pressure in the system, and other factors influencing the conditions for internal and external diffusion. The key stages of metal oxide reduction and the contribution of each mechanism to the overall reduction process depend on the balance of these factors.

The reduction of metal oxides from liquid slags with carbon can occur through direct interaction. This mechanism is called direct reduction; it is similar to the process of metal cementation from aqueous solutions and can be accompanied by the exchange of oxygen ions and electrons between the metal oxide and the reducing agent. X-ray observation of the reduction of iron oxide with solid carbon showed that direct reduction occurs only during the initial phase of their interaction. The carbon is then coated with a gas film, which disrupts the contact between the carbon and the slag, and the direct reduction process virtually ceases. The process then continues similarly to the reduction of solid oxides involving the gas phase.

The presented material on the mechanism of the process of reduction of metal oxides and its critical analysis showed that, despite numerous studies conducted in this area, there is no consensus on the mechanism of reduction yet, however, the general trend in the development of ideas on the mechanism of reduction of metal oxides indicates a convergence of previously existing ideas and the need to create a unified theory of the process.

Conclusion

The possibility of reduction processes accompanied by the release of oxygen into the gas phase has been experimentally confirmed.

The experimental results also confirmed the possibility of ion dissociation of iron oxide with the release of negatively charged oxygen ions into the gas phase during its reduction by metallic titanium using a non-contact method.

It was established that the reduction process can proceed via different mechanisms depending on the external conditions, as well as the properties of the oxides and the reducing agents used.

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