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Magnesium Reduction of Titanium Tetrachloride

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Abstract—The reasons for the slow rate of reaction between $TiCl_4$ vapor and a clean Mg surface are clarified, and the role of the magnesium reduction of titanium chlorides in the gas phase and liquid magnesium chloride film is discussed. The mechanisms for the formation of spongy titanium and its deposition on the walls of commercial reactors are elucidated. A continuous procedure is proposed for the preparation of titanium powder.

INTRODUCTION

The magnesium reduction of titanium tetrachloride, $TiCl_4$, a major process for the commercial-scale production of titanium metal, has been studied in great detail. The results obtained by optimizing the procedures for the reduction of $TiCl_4$ with magnesium and sodium are summarized in [1].

Despite the many years of optimization, the procedure most widely used industrially is not free of serious drawbacks, such as batch operation, incomplete use of magnesium, nonuniform quality of the resulting titanium sponge, high energy cost since the process includes vacuum separation and melting of the titanium sponge, and the long time required to prepare the reactor for heating and cooling and to withdraw the titanium sponge.

The use of batch reactors in the magnesium reduction process is associated with the fact that the reaction between $TiCl_4$ vapor and liquid magnesium yields titanium sponge deposited on the reactor wall, which can only be withdrawn after suspending the process and cooling the reactor.

Numerous attempts were made to develop a continuous procedure for the magnesium reduction of $TiCl_4$. Garmata *et al.* [1] refer to more than 80 patents and papers devoted to continuous procedures for producing titanium via sodium or magnesium reduction of $TiCl_4$. In spite of the considerable research effort in this area, devising a continuous procedure for the magnesium reduction of $TiCl_4$ remains a challenge, possibly because the mechanism of the reaction between magnesium and titanium tetrachloride has not yet been studied in sufficient detail.

THEORY

Analysis of the published data on the mechanism of the magnesium reduction of titanium tetrachloride and the theoretical and experimental studies carried out at the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, and the Institute of New Chemical Problems, Russian Academy of Sciences, made it possible not only to gain a more detailed insight into the chemistry of the magnesium reduction of $TiCl_4$ vapor but also to establish conditions for continuous production of monodisperse titanium powder suitable for powder metallurgy and the manufacture of cast Ti and Ti-base alloys.

The mechanism of chemical interaction between $TiCl_4$ and Mg is difficult to clarify in detail because the reduction of $TiCl_4$ is a multistep process and also because, at high temperatures, the reaction may occur not only on the surface of molten Mg but also in the gas phase and in the liquid magnesium chloride film covering the Mg surface, titanium sponge, and reactor wall. The process is also influenced by chemisorption, the vaporization and dissolution of magnesium and titanium chlorides in liquid magnesium chloride, the nucleation and growth of titanium particles, and electrochemical phenomena inherent in redox reactions. The mechanism of this heterogeneous process appears to be too complex to be clarified by conventional chemical means.

The purpose of this study was to identify the factors responsible for the formation of titanium sponge and titanium deposition on the reactor wall in order to establish the conditions suitable for continuous preparation of titanium.

To this end, we studied the role of each elementary process by comparing the rate of the reaction between titanium tetrachloride and liquid magnesium with the rates of gas-phase reactions and the reactions in the liquid magnesium chloride film.

Since the contributions of parallel reactions to the overall reaction rate cannot be determined experimentally, the rates of the gas-phase reactions and the reaction between $TiCl_4$ and liquid Mg were evaluated theoretically.

In assessing the rate of the reaction between $TiCl_4$ vapor and a clean surface of molten magnesium, we relied on the theory of rate processes (steady-state theory) [2]. According to this theory, for a chemical reaction to occur, not only the reactant molecules should approach one another closely enough but also the parameters of the molecules in the gas phase should match in a certain way those of the condensed phase.

This theory makes it possible to assess the probability and effectiveness of the collisions of gaseous molecules against the surface of the condensed phase and to evaluate the barrier heights and reaction rates involved using data on the geometry and properties of the reactant particles ($TiCl_4$ molecules and Mg surface).

Consider the interaction between titanium tetrachloride molecules and the surface of liquid magnesium. The $TiCl_4$ molecule has the shape of a tetrahedron, with the Ti atom residing in the center position and the Cl atoms sitting in the vertices. The Ti–Cl distance in the $TiCl_4$ tetrahedron is 2.18 Å, and the angle at vertex is 109°, so that the Cl–Cl distance is 3.6 Å. Crystalline magnesium has a hexagonal structure, with an Mg–Mg bond distance of 3.2 Å. In molten magnesium, the interatomic distance is 15–20% larger.

The full structural match (necessary for chemical interaction) between the $TiCl_4$ molecule and the surface of liquid magnesium is only achieved if one of the faces of the $TiCl_4$ tetrahedron (equilateral triangle with a side length of 3.6 Å) is parallel to the liquid surface and the three Cl ions are situated directly over three Mg atoms.

It is only in this configuration that a collision of a $TiCl_4$ molecule against the Mg surface may result in the formation of three bonds, leading to strong chemisorption and a reaction between titanium tetrachloride and magnesium.

The probability of such a collision is extremely low. All the other types of collision (with a vertex or edge coming in contact with the surface) are more likely but do not ensure the formation of three bonds and are, hence, less effective. The low probability of effective collisions and the low effectiveness of the other collisions account for the slow rate of the reaction between $TiCl_4$ and the Mg surface.

The calculation results lead us to conclude that a clean surface of liquid magnesium is essentially nonreactive with titanium tetrachloride. Therefore, to explain the low initial reaction rate, there is no need to assume that the Mg surface is covered with a film preventing chemical interaction, as was done in many studies.

In assessing the rate of the reaction between titanium tetrachloride and a clean surface of liquid magnesium in an industrial reactor, the following assumptions were made: All the sites on the magnesium surface are active (unoccupied); if an incident $TiCl_4$ molecule has one of its faces parallel to the surface (full structural match), the collision effectiveness is 100%. At low surface coverages, the density of active sites is almost constant. Under these assumptions, the reaction is first-order, and its rate is proportional to the $TiCl_4$ concentration in the gas phase.

It follows from our calculations for typical conditions of industrial processes that, if the only reaction were the one between $TiCl_4$ molecules and a clean surface of liquid magnesium, it would take 2450 h for the $TiCl_4$ pressure in the reactor to decrease from 10^5 to 0.9×10^5 Pa. Because of the decrease in the density of active sites on the magnesium surface upon the formation of Mg–Cl bonds, the rate of the reaction between $TiCl_4$ and the surface of molten Mg should be even lower. Taking into account the other types of collision (the surface impacted by a tetrahedron edge or vertex) reduces this period of time by about one order of magnitude, but still the initial reaction rate is much faster than the actual one.

In the initial stages of the process, a more important part is played by the gas-phase reactions between titanium chlorides and Mg vapor. The predominance of gas-phase reactions is evidenced by the fact that, in the initial stages of the exothermic reduction process, the temperature is maximal some distance away from the magnesium surface [3].

Since the probability of triple collisions is low, the gas-phase reactions yield lower titanium chlorides, magnesium chloride, and magnesium subchloride. The rate of reaction between $TiCl_4$ molecules and Mg vapor was calculated for the processes

$$TiCl_4 + Mg = TiCl_3 + MgCl,$$

$$TiCl_4 + Mg = TiCl_2 + MgCl_2.$$

The activation energies and rates of these reactions are difficult to assess theoretically [4]. Semiempirical estimates led us to conclude that their rates are rather high. At 1000 K, the rate-limiting process is magnesium vaporization. The formation of stable Ti nuclei as a result of gas-phase reactions appears unlikely because there is no uncombined titanium in the gas phase, despite the high supersaturation with Ti.

The formation of a liquid magnesium chloride film on the Mg surface impedes Mg vaporization, thereby reducing the rate of gas-phase reactions, as evidenced by the fact that the maximum in temperature shifts to the Mg surface.

The reactions occurring in the liquid magnesium chloride film by the vapor–liquid–solid mechanism seem to play a key role in the deposition of spongy titanium on the reactor wall.

That a chloride film on the metal surface may not only retard but also substantially accelerate interaction between the metal and gas phase was shown by measuring the temperature-dependent rate of reaction between

Granulometric composition of titanium powder (sieve analysis)

Sample no.	Percent of size fraction	
	from –0.4 to +0.1 mm	from –0.1 to +0.05 mm
1	86.6	13.4
2	90.2	9.8
3	88.4	11.6

tin tetrachloride and the surface of liquid tin. The reaction rate was found to drop rapidly above the boiling point of tin dichloride owing to the disappearance of the film [5].

A necessary condition for a reaction to occur in a liquid film is the dissolution of the reactants in the film.

To achieve high rates of Ti formation in a liquid magnesium chloride film, not only high solubility of Mg and titanium chlorides in liquid $MgCl_2$ but also the presence of a solid substrate are essential, because the substrate makes it possible to avoid difficulties associated with the formation of stable titanium nuclei.

According to Bukun and Ukshe [6], Mg solubility in $MgCl_2$ between 800 and 1200°C is 0.25–0.40%. The solubility of titanium chlorides is substantially higher and is sufficient to ensure high reduction rates of the titanium chlorides in the liquid magnesium chloride film.

Before the formation of stable titanium nuclei, the titanium resulting from the reduction of $TiCl_4$ may deposit on any solid substrate wettable by liquid magnesium chloride (reactor wall or titanium sponge).

It is safe to assume that the liquid $MgCl_2$ film not only does not inhibit the reduction process, as is commonly believed [7], but also accelerates it because it is in this film (on titanium sponge, titanium nuclei, or reactor wall) that titanium is formed preferentially.

The deposition of titanium on the reactor wall and the formation of spongy titanium can be avoided by reducing $TiCl_4$ under conditions that preclude contact between Mg and the reactor wall, e.g., on the surface of liquid Mg jetting vertically through $TiCl_4$ vapor.

This method is based on the fact that the rate of reaction between $TiCl_4$ and a clean Mg surface is rather low but increases markedly upon the formation of titanium nuclei as a result of the reactions in the $MgCl_2$ film. For this reason, the reduction of titanium chlorides will occur, for the most part, on the surface of the titanium particles present in the liquid Mg jet.

As a result of Mg circulation, Ti particles will repeatedly appear in the reaction zone, come in contact with titanium chlorides, and increase in size. Under the effect of gravity, large Ti particles will settle to the bottom of the reactor, to below the layer of $MgCl_2$, which has a higher density as compared to liquid Mg and, for this reason, collects below it. Thus, the growth of Ti nuclei is accompanied by powder classification.

Under these conditions, Ti deposition on the reactor wall is unlikely because the Mg does not come in contact with the wall.

EXPERIMENTAL

In our experiments, we used a bench-scale reactor incorporating a resistance-heated 4-l melter; a vertical reaction chamber 600 mm in height, secured to the lid of the melter; and a centrifugal pump, which produced a vertical jet of molten metal. In preliminary runs, we used water to adjust the jet so that it would not reach the wall or lid of the reaction chamber.

After magnesium was melted and heated to 780°C in the melter, the pump was switched on, and $TiCl_4$ vapor was introduced into the reactor through an inlet hole in the lid at a rate adjusted in such a way that the temperature was maximal in the upper part of the melt jet. By varying the process parameters, we found conditions ensuring the preparation of titanium powder.

A series of test runs was also carried out using a pilot-scale setup incorporating a reactor, melter, and receiver for reaction products (liquid magnesium chloride containing titanium powder). Liquid magnesium (1200–1300 kg) was loaded into the tank (800-mm diameter, 1900-mm height) of the reactor, equipped with a reaction chamber (530-mm diameter, 3400-mm height) and centrifugal pump. After heating to 780–820°C, the pump was switched on. The jet height was 2.6–2.9 m. $TiCl_4$ vapor was introduced into the reactor through the lid of the reaction chamber at such a rate that all the $TiCl_4$ reacted with the upper part of the melt jet. The reaction products (magnesium chloride containing titanium powder) were withdrawn every 3–4 h, and the same volume of liquid magnesium was introduced again into the tank.

The granulometric composition of the resultant Ti powder is presented in the table.

CONCLUSION

A continuous process was proposed for the preparation of titanium powder via magnesium reduction of titanium tetrachloride. The process was tested using bench- and pilot-scale reactors. The results can be used to design a commercial-scale reactor.

The process is several times cheaper than the existing processes and will significantly extend the application field of powder metallurgy techniques for the production of titanium parts.

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