

The Continuous Production of Titanium Powder Using Circulating Molten Salt

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Author's Note: Santa Fe Alloys and G.R.B. Elliott have had extensive experience with presumably similar continuous uranium production from molten salt, but their experience with titanium is limited. Therefore, this paper should be read with the understanding that inadvertent errors may have resulted from that inexperience. Until further experimental information validates the theoretical concepts here proposed, the paper's contents should be viewed as hypotheses.

INTRODUCTION

A well-known goal in the titanium industry is the development of a continuous technology to produce cheaper and better titanium. As a possible step toward this goal, the TiLAC™ chemistry¹ developed at Santa Fe Alloys could avoid the costs of the multiple furnace evacuations in the Kroll process; further, the presence of metallic impurities from the starting $TiCl_4$ could be reduced. TiLAC is designed to allow the excellent physical separation of its titanium product from small amounts of the melted salt. Such removal is very difficult with Kroll. Also, continuous operations with TiLAC could offer significantly lower

labor costs and reduced capital costs, as compared with Kroll. These considerations appear to offer \$2/lb. savings or more over the \$7/lb. price for the Kroll process.

Several new processes, some with considerable merit that address several areas of need, were discussed at the Titanium Industry Workshop, held in July 1997 at Welches, Oregon.² The concept closest to TiLAC is a molten salt process^{3,4} from Albany Research Center, Oregon, and independent cooperators. In one Albany usage, a stream of molten salt holds a $TiCl_2$ -NaCl solution, and a second holds a Na-NaCl reducing solution. These streams meet in a stirred reactor, where granular titanium can be supported and grown to a desired approximate size. TiLAC, in contrast, reduces with magnesium that is insoluble in molten salt. Other potentially useful new processes are now being offered on long-sought vapor-phase (or gas-suspended) reduction (e.g., $TiCl_4$ with sodium or magnesium). There are also processes offered with the use of quenches of plasma and hydrogen.^{3,5} Continuous ingot production may be incorporated also.^{6,7}

THE TiLAC PROCESS

The TiLAC process¹ is shown in Figure 1. A modified block diagram shows two main regions—stages one and two—that carry out the titanium production. To avoid the Kroll process's sponge sintering reaction ($TiCl_4 + 2Mg = Ti + 2MgCl_2$), the TiLAC process is broken into two reactions that can run smoothly (i.e., the reactions listed in Figure 1 under stages one and two).

Kroll's chemical reactions occur by direct contact; $TiCl_4$ must bump magnesium even though melted salt tries to keep them apart. The TiLAC solution has a designed chemistry and structure that encourages electrochemical reactions, like microscopic batteries. The stage one electrochemical reaction, for example, may proceed smoothly even if the magnesium and $TiCl_2$ are not close—if the battery is set up.

The stage two reaction is also designed to be electrochemical. The reaction has the capacity to reject impurities that would otherwise go into the titanium that is being formed. Such impurities might be brought in from the starting $TiCl_4$ or through the possible recycling of titanium scrap.

Within the block of stage one, two lines of waves indicate a layer of melted magnesium that floats on a melted mixture of magnesium chloride and potassium chloride, $MgCl_2$ -KCl. Melted salts fill the lower part of the container (except for the titanium product sunk to the bottom). The arrows in Figure 1 show the movement of material. Likewise, within the block of stage two there is a single wave that indicates that the melted salts fill that box.

Following the stage one reaction, titanium product forms at $\sim 750^\circ C$ as flowing titanium feedstock in melted salt ($TiCl_2$ - $MgCl_2$ -KCl) reacts with melted magnesium that floats on $TiCl_2$ -free melted salt. The salt now holds extra $MgCl_2$ from the stage one reaction by-product. The titanium product settles and is removed mechanically from the container bottom. The by-product $MgCl_2$ dissolves in the flowing melted salt; later, an equal amount of $MgCl_2$ is

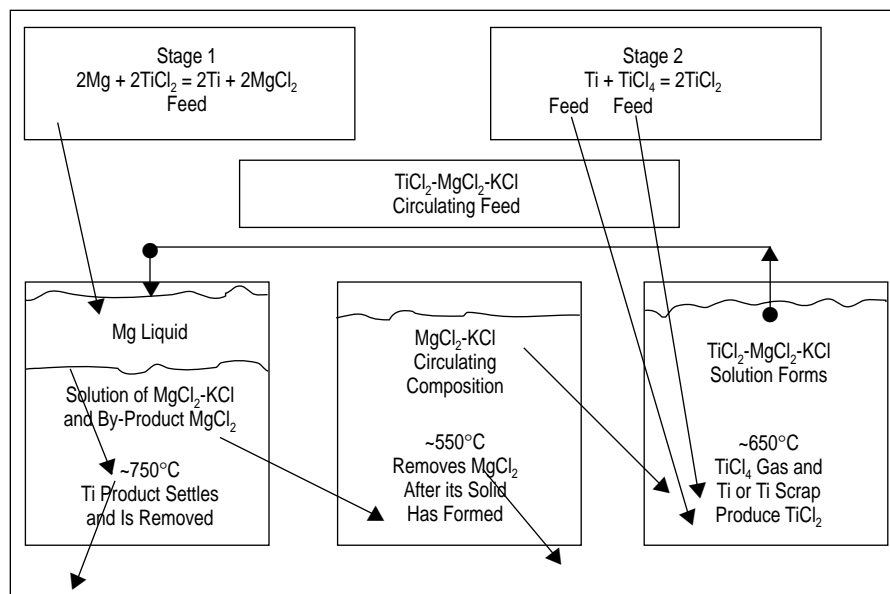


Figure 1. The TiLAC process for continuous production of titanium from flowing molten salt.

solidified out of the flowing salt by cooling along a $MgCl_2$ liquidus curve. The by-product is recycled (e.g., by $MgCl_2$ electrolysis). The feedstock is regenerated as melted salt passes through a region where titanium lying on the bottom reacts with flowing gaseous $TiCl_4$, thereby following the stage two chemical reaction. $TiCl_2$ - $MgCl_2$ - KCl forms and moves on to stage one.

ECONOMICS AND MARKET POTENTIAL

Major use of the TiLAC product is possible if the product is suitable for immediate melting to ingot or for powder processing to near-net shapes, possibly at \$6/lb.

The technical improvements and monetary value added by TiLAC vs. Kroll processing will not really be known until experiments and production establish the TiLAC quality and its ability to satisfy the special needs of users.

Cost comparisons are not easy. Baburaj and Froes⁸ use the following costs:

- Titanium sponge: Japanese premium grade, \$4.60/lb.; Russian, \$3.90/lb.
- Titanium powder: Chinese sodium reduced, \$15/lb.; hydride/dihydride (PAC), \$40.00/lb.

In general usage, Kroll sponge is valued at ~\$4.25/lb. after it has been cleaned by hot evacuation but has not been melted. The cost ranges suggest the sort of added value that may be gotten for reductions that avoid Kroll. The added value may vary wildly.

The Chinese sodium reduction includes the intermediate manufacture of $TiCl_2$. This intermediate occurs in other sodium reductions of $TiCl_4$ (e.g., the Hunter process and Gerdemann).³ TiLAC uses the formation of this same intermediate, $TiCl_2$, as a special cleaning process to eliminate many metallic elements from $TiCl_4$ and from recycled titanium that will be converted to the TiLAC product.

In this way, TiLAC has important business potential in special niche markets.

These will have to be evaluated in the near future. Steadily growing, expandable markets have been predicted by Aguirre⁹ and Katrak.¹⁰

In regard to energy, environment, and capital expenditures, TiLAC seems promising. TiLAC magnesium is entirely consumed for the product, as opposed to Kroll's 25% excess used. Titanium product clean-up is also low-cost and effective, saving the major pumping and heating costs to make sponge into quality ingots. Other significant energy savings will be met in special-needs titanium production. The continuous production in a closed glove box with inert-gas atmosphere conserves energy. The upgrade of titanium scrap to TiLAC quality is another area of potentially significant savings. However, large projects (e.g., Mg - $TiCl_4$ gas phase reactions moving directly to billets) may save more energy than TiLAC while providing a much-improved product over the one produced by Kroll.

All reactants are consumed and all by-products are recycled in the TiLAC process. The by-product $MgCl_2$ is removed as a clean solid that should not require additional processing before electrolysis recycle. The Kroll hazards are presumably avoided. These continuous units are also capable of being used by small operations. Continuous operations usually can readily exceed the outputs of clumsy batch operations. The equipment is simple.

KEY EXPERIMENTAL RESULTS

Santa Fe Alloys has experimentally validated the concept that molten magnesium will reduce Ti^{++} and Ti^{+++} dissolved in molten salts as they pass by the magnesium, as in stage one (Figure 1). Likewise, Ti^{++} and Ti^{+++} can be returned to molten salt by reactions of titanium powder and titanium tetrachloride in the presence of molten salt, holding further Ti^{++} and Ti^{+++} in molten salt.

An argon-filled glove box attached to nesting alumina-, quartz-, and copper-closed tubes filled with argon was used

with the tetrachloride. The bottom of the nest was in a furnace below. A peristaltic pump circulated argon gas carrying $TiCl_4$ vapor deep into a molten salt ($MgCl_2$ - KCl) solution in a copper container holding titanium in the bottom at ~600°C. This generated a solution of $TiCl_2$ - $MgCl_2$ - KCl , which was cooled and opened in the glove box.

Another closed alumina tube in the furnace and attached to the glove box was loaded with melted $MgCl_2$ - KCl ; magnesium was added to make a molten layer. Pieces of the cooled $TiCl_2$ - $MgCl_2$ - KCl were added into the molten salt to yield titanium precipitate in the bottom of the salt. No further examination was done at the time.

FUTURE DEVELOPMENT

Much more experimental work is planned. Systems will be set up to test both stages one and two and see what characteristics give the best products. Once a suitable product is attained, the stages will be joined into a system that can run continuously.

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