

# THE ANALOGY AND DIFFERENCES BETWEEN ALUMINIUM AND TITANIUM ELECTROWINNING

DS van Vuuren<sup>1</sup>, AD Engelbrecht, TD Hadley

<sup>1</sup>Materials Science and Manufacturing, CSIR

Correspondence to: DS van Vuuren, Materials Science and Manufacturing, CSIR, PO Box 395, Pretoria, 0001, Tel: +27 12 841-2375, Fax: +27 12 841 2135, E-mail [dvvuuren@csir.co.za](mailto:dvvuuren@csir.co.za)

## Abstract

Titanium is the ninth most abundant element and the fourth most common construction metal in the earth's crust. Its high strength, high-temperature performance, low density, high corrosion resistance and bio-compatibility makes it the ideal materials choice in a wide variety of applications. However, the global production and use of titanium are very small due to its high cost of production.

Since 1946 when the titanium industry began to evolve following the commercialisation of the Kroll process, many attempts had been undertaken to reduce the cost of producing titanium. To date all the attempts failed commercially and only the Kroll and to a lesser extent the earlier Hunter processes are used commercially.

One of the numerous process alternatives considered is electrowinning of molten titanium in an analogous way to aluminium electrowinning. This process is conceptually very attractive and if successful could provide the cost breakthrough required to make titanium affordable to a much larger market.

The authors have tested this route experimentally, but could not produce pure titanium. The failure of electrowinning pure, molten titanium has been interpreted in terms of the analogy and differences between aluminium and titanium electrolysis resulting in a clear understanding of the fundamental obstacles that have to be overcome in order to develop such a process successfully.

## Keywords

Titanium, titanium dioxide, electrowinning, molten salt

## Introduction

Titanium has unique chemical (corrosion-resistance) and physical properties (strength-to-weight ratio in particular) that make it a highly desirable for use in a number of industries (e.g., the aerospace, chemical, automotive and construction industry). However, because of its high price (about US\$ 8.0/kg for sponge and US\$12-20/kg for ingot) its current market share is only about 80 000 tonnes per annum, mostly in the aerospace industry. The high price of titanium metal is not a result of its scarcity, in fact it is the fourth most abundant structural metal in the earth's crust, it is a consequence of the antiquated technology used for the extraction of the metal from its raw materials. Therefore, to unlock the market for titanium metal it is necessary to develop new technology that will drastically reduce the production cost of the metal. In this regard it has been estimated<sup>1</sup> that the price / demand relationship for titanium follows the "1-10-100 rule", which observes that a \$1/pound reduction in sponge cost, combined with a 10% reduction in mill production cost (value added in melting and primary fabrication) should lead to a 100% increase in the demand for titanium in non-aerospace applications.

Numerous attempts were undertaken in the last 60 years to reduce the cost of producing titanium. Excellent reviews, e.g. Hartman *et al*<sup>2</sup> and Turner *et al*<sup>3</sup> are available on past developments; and a comprehensive survey of current work has been undertaken recently by ERKTechnologies<sup>4,5</sup> on behalf of the DOE and Oak Ridge National Laboratories.

Comparing the economics of alternative process routes is difficult since the value of the final product is highly dependent on the form and quality of the titanium produced. For example, it has been reported that titanium powder from various parts of the world costs \$18 to \$440/kg<sup>6</sup> depending on quality. This large variation in potential value becomes overriding in any techno-economic analysis of alternative routes.

However, the value chain of producing titanium provides some perspective. The cost built-up for producing titanium via the Kroll process is approximately as follows:

- Ilmenite \$0.27/kg Ti sponge
- Titanium slag \$0.75/kg Ti Sponge
- TiCl<sub>4</sub> \$3.09/kg Ti Sponge
- Ti Sponge raw materials costs \$5.50/kg Ti Sponge
- Total Ti Sponge cost \$8-\$11/kg Ti Sponge
- Ti ingot \$12-20/kg Ti

Considering the cost built-up, it is clear that significant potential exists (in excess of \$9/kg) to reduce costs, if molten (or castable) titanium can be produced directly from TiCl<sub>4</sub>. Whereas pure TiO<sub>2</sub> costs about the same as TiCl<sub>4</sub>, the same margin exists to reduce the cost of titanium when using TiO<sub>2</sub> as feedstock.

The concept to electrowin molten titanium from titanium dioxide has been proposed and tested by a number of groups. Specific previous studies in this regard are:

- The earliest work found in the literature is that of Hashimoto *et al*<sup>7</sup> in 1971. Hashimoto *et al* proved the principle, but were unable to produce product meeting industrial titanium specifications.
- Two early patents in this field disclose a process conceived by Donahue *et al*<sup>8,9</sup>. Donahue and his co-workers described a method and apparatus to produce molten titanium electrolytically via a DC plasma cell.
- Takenake *et al*<sup>10,11</sup> used a DC-ESR (Direct Current Electro Slag Remelting) apparatus to reduce TiO<sub>2</sub> to liquid titanium. Takenake reported results with very low oxygen and carbon contents.
- Sadoway<sup>12</sup> patented the principle to use a consumable titanium oxide anode that becomes electrically conductive at high temperatures.
- Larson *et al*<sup>13</sup> described an experiment using a plasma as anode avoiding direct contact of carbon with the electrolyte.
- Cardarelli<sup>14</sup> disclosed an electrolytic process to recover molten titanium directly from titanium oxide containing compounds such as TiO<sub>2</sub>, ilmenite, leucoxene, perovskite, slag etc.

An electrochemical process producing molten titanium directly from TiO<sub>2</sub> has the following advantages:

- Less process steps
- Continuous operation
- Higher energy efficiency
- De-linking titanium production from TiCl<sub>4</sub> and Mg or Na production. Similarly to aluminium production, the electrolysis plant does not have to be close to the raw material plants
- Non-hazardous feed material that is easily transported and stored (TiO<sub>2</sub> vs TiCl<sub>4</sub>)
- Alternative feed supply (TiO<sub>2</sub> from either the chloride or sulphate routes).

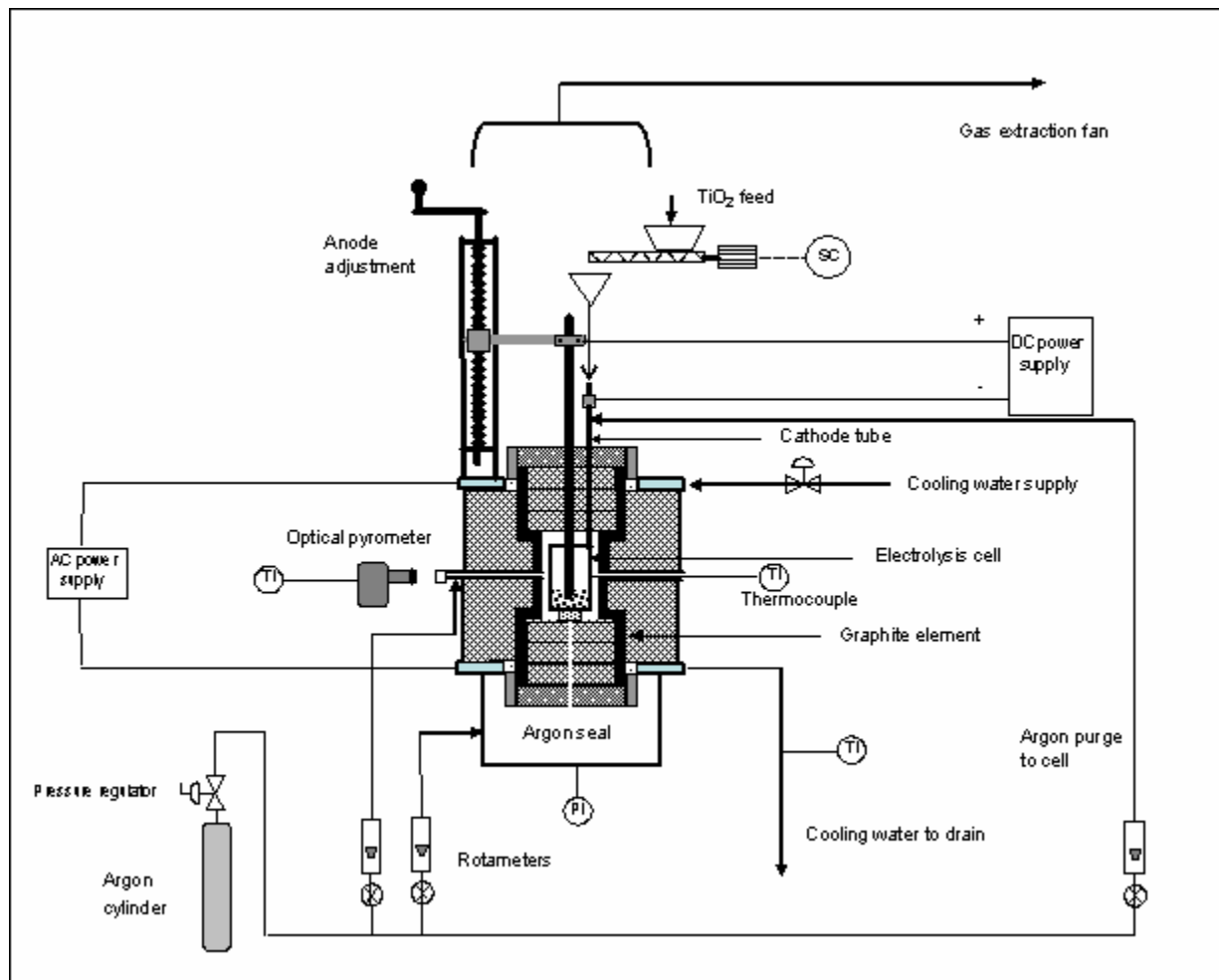
## Experimental

A drawing of the bench scale electrolysis cell and apparatus is given in Figure 1. The electrolysis cell is heated

by means of an AC graphite tube furnace rated at 35 kW. Power is supplied to the water-cooled lid sections of the furnace. Electrical contact between the lid and the graphite tube element is achieved by means of granular carbon placed in a ring gap around the end section of the graphite element. The central section of the furnace can reach temperatures of 2200°C. Argon is continuously purged into the furnace from the bottom to prevent oxygen from entering the furnace and reacting with the element.

The electrolysis cell consisted of a graphite crucible, lined with molybdenum sheeting along the bottom and side of the cell. A close-fitting graphite lid was used to close the cell and a graphite anode protruded through a graphite tube inserted into the lid into the cell. The anode was electrically isolated from the graphite tube and hence the cell. The direct current used for electrolyzing the cell contents was supplied via electrical connections to the graphite anode and the graphite cell that formed the cathode via the molybdenum lining.

**Figure 1: Bench Scale High Temperature Electrolysis Apparatus**



The electrolysis cell is placed in the central section of the element. This central section of the furnace element has two 12 mm holes that are used to measure the temperature by means of an optical pyrometer and a tungsten rhenium thermocouple. The optical pyrometer is calibrated against the tungsten rhenium thermocouple. Argon is supplied to the optical pyrometer view port in order to keep the Pyrex viewing glass clean. The temperature of the cell is controlled by manual adjustment of the AC power supply.

The anode is adjusted manually by means of a rotating threaded rod as the carbon is consumed by the reaction. The cathodic contact with the cell is achieved by means of a graphite (cathode) tube screwed into the lid of the cell. The cathode tube is also used to purge the cell with argon and to feed  $\text{TiO}_2$  to the cell.

Vapour emitted from the cell is extracted by means of an extraction hood placed above the furnace.

The internal dimensions of the cell were:

Diameter:	80 mm
Height:	120 mm

In most of the experiments  $\text{CaF}_2$  was used as the electrolyte, but in some  $\text{BaF}_2$  was added to increase the density of the electrolyte in an attempt to prevent particles of carbon that might have broken off from the anode to sink into the electrolyte. The electrolyte height was approximate 30 mm in all experiments.

The following experimental parameters were varied:

- Temperature: 1750 to 1800°C
- $\text{TiO}_2$  concentration: 6% to 20%
- Current densities: 10 to 60  $\text{kA/m}^2$  at the anode and 2.5 to 5  $\text{kA/m}^2$  at the cathode
- Anode diameter: 25 to 40 mm
- Start-up and shut down procedures
- Anode to cathode voltage: 1.1 to 3 V (up to the time of when the cell resistance increased on depletion of dissolved  $\text{TiO}_2$ ).

The experimental procedure was loading the cell, flushing it with argon, heating the system to the desired operating temperature over a period of about 6 hours and then lowering the anode until it made electrical contact with the molten electrolyte.

The system was in most cases run at a fixed current. During the experiments the voltage gradually increased as the  $\text{TiO}_2$  concentration in the electrolyte decreased and as the anode became consumed. The anode was therefore lowered from time to time to compensate for its consumption. After a couple of hours, the measured voltage became unstable and jumped to 5V (the maximum set).

This effect is known in the aluminium industry as the anode effect and is ascribed upon depletion of alumina in the electrolyte to the formation at the anode of  $\text{CF}_4$  that increases the resistance between the anode and the electrolyte. In some of the experiments, the electrolysis was continued for a couple of hours after observing the anode effect. In these experiments, the power supply operation was then changed to a fixed voltage mode rather than a fixed current mode.

At the end of each run the cell temperature was reduced at  $\pm 5^\circ\text{C}/\text{min}$  while maintaining the applied voltage between the anode and the cathode. Once the temperature dropped to below about  $1600^\circ\text{C}$ , the anode was lifted above the electrolyte surface and the system cooled to room temperature. Once cooled, the contents of the cell were removed, examined and analysed by XRD, chemical analysis and SEM analyses.

## Results

In all the experiments a granular product was formed that settled to the bottom of the cell. Figure 2 is a photograph of the cell contents collected after an experiment.

**Figure 2: Typical Electrolysis Product Deposit**



In most cases the product collected had a brown colour, but in some cases it was dark grey. Depending on how long the voltage was applied after the cell resistance started to increase and on experimental conditions, the colour of the electrolyte layer on top of the product varied from white to light blue and even light pink.

The analyses of a typical sample and of the range measured for all the experiments are given in Table 1:

**Table 1: Chemical analysis**

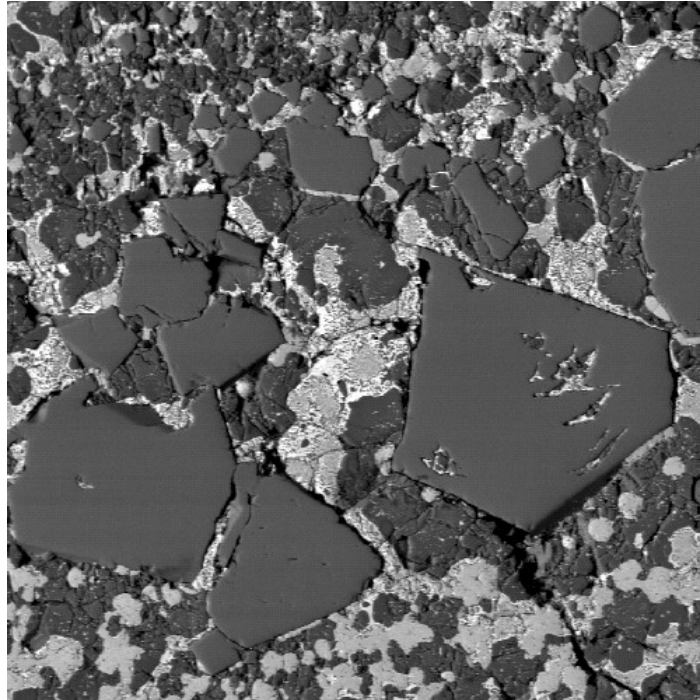
	Layer at bottom of the cell			Top electrolyte section		
	Ti (%)	C (%)	Ti/C (mol ratio)	Ti (%)	C (%)	Ti/C (mol ratio)
Typical	13.30	1.59	2.09	1.41	0.04	8.19
Range	7.9 – 14.5	0.78-1.8	1.8-2.5	0.25-1.6	0.02-0.07	0.06-20

XRD analysis showed in all cases that the bulk of the titanium product was either Hongquite (TiO) or TiC. The differences between the XRD patterns for different TiO and TiC standards are so small that it was not possible to conclude from the XRD measurements alone whether the product was TiO or TiC. From the chemical analyses, the product contained about 50% TiC, hence it is possible that the product was a mixture of TiC and TiO. It is also possible that the product contained  $Ti_2C$ , but this was not indicated by the XRD analyses.

Figure 3 shows a SEM image of one of the more crystalline product samples produced. Little evidence was found of producing a molten product that coalesced.



**Figure 3: SEM Image of Crystalline Product**



Another unexpected result was that gas bubbles formed at the cathode. Figure 4 is a photograph of one of the product samples clearly showing the pores caused by bubbles at the cathode. In later experiments, it was found that when the previously thought anode effect occurred, lowering of the applied voltage to below about 1.5V, the cell current **increased**. Increasing the voltage to above about 1.6V reversed the trend causing a rapid decrease in current. It was therefore concluded that it was not an anode effect, but rather a cathode effect associated with the evolution of gas at the cathode causing a sharp increase in the cathode to electrolyte resistance.

**Figure 4: Bubbles Formed at the Cathode**



## Discussion

### Failure to Produce Molten Titanium

The spherical particles formed in the process were ascribed to titanium dioxide becoming reduced to form a lower oxide with a lower melting point and a lower melting solubility in the slag. The melting point of  $Ti_4O_7$  is  $1677^\circ C$ , which is well below the operating temperatures used. As the  $Ti_4O_7$  became further reduced it formed  $TiO$  with a melting point of  $1750^\circ C$ . When reducing or deoxidising  $TiO$  further, the melting point of the solid increases to a peak value of about  $1900^\circ C$ . This is much higher than the maximum temperature of  $1800^\circ C$  used in the work.

Hashimoto *et al* found similar results and showed that when increasing the cell operating temperature above  $1800^\circ C$ , they could produce an ingot instead of a granular product.

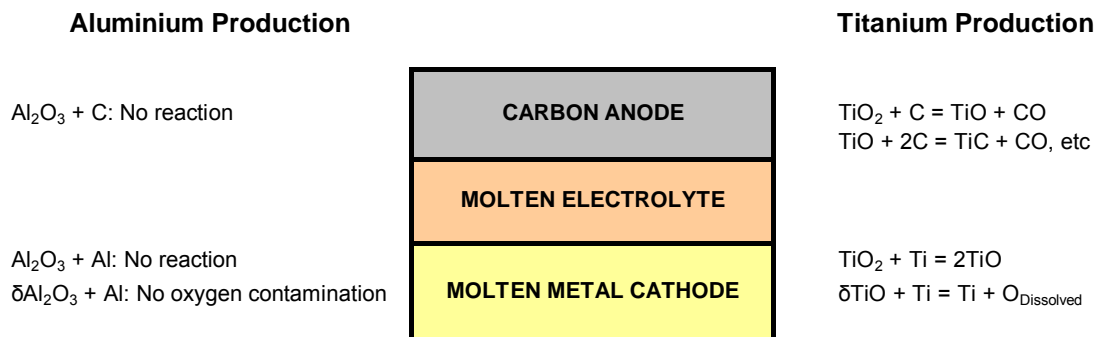
Takenake *et al* also reported the formation of a molten product when using an electric arc at the anode. The temperature in their cell presumably rose sufficiently to overcome the problem of the high melting point of intermediate lower titanium oxide species.

### Failure to Prevent Titanium Carbide Production

Assuming that the oxidation state of titanium in titanium carbide is +2, it is theoretically possible to decompose titanium carbide into titanium and carbon if an electric potential of more than 0.82V is applied to a solution of titanium carbide in an electrolyte at  $1700^\circ C$ . It should therefore be possible to prevent the formation of titanium carbide in the first instance if a voltage of more than 0.82 V is applied between the cathode and the carbon anode of a titanium oxide electrolysis cell. However, formation of  $TiC$  could not be prevented in the experiments in spite of conscious efforts in especially the later experiments to make sure that high (more than 1V) voltages were applied to the electrolytic cell throughout the duration of the experiments.

In order to understand this negative result, it is useful to compare the proposed titanium electrolysis process with the standard Hall-Hérout aluminium production process. Figure 5 is a diagrammatic representation of an electrolysis cell illustrating some key differences between the two processes.

**Figure 5: Schematic Comparison of Alumina and Titania Electrolysis**



As shown on the left hand side, dissolved alumina does not react with the carbon anode, even if no potential is applied between the cathode and the anode. In actual fact, the cells are lined with graphite that is in direct contact with the molten aluminium produced. In contrast, at the temperature of operation, all titanium oxides react spontaneously with carbon to firstly produce lower titanium oxides and finally titanium carbide.

The electric potentials applied in the experiments were not sufficient to prevent the reaction between dissolved titanium oxides and carbon. Considering that the anode current densities used was in the order of  $3 \text{ A/cm}^2$ , assuming that the current efficiency was 50%, and the dissolved  $\text{TiO}_2$  concentration only 1% in the electrolyte, the velocity of oxygen ions to the anode was only about  $100 \text{ }\mu\text{m/s}$ . The velocity of convection currents in the cell could easily have been in the order of  $1 \text{ cm/s}$  with the result that mass transport due to convective mixing was much faster than the mass transport due to the applied electric potential. Consequently, in addition to the electrochemical reaction between carbon and oxygen anions, carbon could have reacted spontaneously with the dissolved titanium oxide to produce titanium carbide.

Another possible cause for the formation of titanium carbide is carbon dissolving in the electrolyte and subsequently reacting with titanium. No literature data could be found on the solubility of carbon in calcium or barium fluoride, but considering the chemical analyses of the used electrolyte samples, the solubility of carbon is very low. The lowest carbon concentration measured was 0.019% and the highest 0.067%. In all the cases the molar concentration of titanium dissolved in the electrolyte far exceeded molar carbon concentration. Considering the high reactivity of titanium and all the titanium oxides with carbon, it was deduced that the bulk of the carbon in the electrolyte was present as dissolved titanium carbide and not as elemental carbon. It was therefore concluded that the predominant source of carbon in the product is from carbon that reacted with the titanium species at or near the anode and not from elemental carbon that dissolved from the anode in the electrolyte and then reacted with titanium at the cathode.

#### Oxygen in the Product

Referring to Figure 5, another major difference between electrowinning aluminium and titanium from their oxides, is the fact that dissolved alumina in the electrolyte does not unduly contaminate the aluminium with oxygen, whereas dissolved titanium oxides in higher oxidation states react with titanium metal to form titanium in a lower oxidation state. The solubility of oxygen in titanium is also very high so that relatively small concentrations of any dissolved titanium oxide species results in excessive oxygen dissolving in titanium.

In order to make the proposed process work continuously, it would therefore always be necessary to run the electrolysis cell at a very low concentration of dissolved titanium monoxide. This would in turn result in very low rates of electrolysis.

#### Gas Formation at the Cathode

As mentioned above, it was found that after reaching the point where the voltage sharply increased in a constant current experiment, that decreasing the cell voltage below about 1.5V resulted in an increase in the current. The decrease in current at higher voltages was ascribed to the formation of gas at the cathode.

It is uncertain what gas is actually formed though it is most likely either carbon monoxide or oxygen. Possible chemical reactions that could lead to the formation of these gases at the cell potentials where the phenomenon was observed are:



and



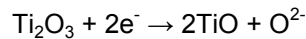
The potential required for deoxidising  $\text{TiO}$  seems a bit too high:



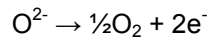


In order for these reactions to occur electrochemically, the anodic reaction must occur in a region slightly above the cathode where the gas bubbles are formed. The electrons given up by the anions forming the gas must be conducted by electronic conduction through the electrolyte to the graphite anode contact. Postulated cell reactions for the deoxidation reaction of  $Ti_2O_3$  are:

Cathode:



Anode:



Although it is uncertain what gas is formed, the evidence indicates that a gas is formed near the cathode, that a threshold voltage is required for such a gas to form and that the electrolyte acts as an electronic conductor to enable the electrochemical formation of a gas at a position deep in the melt near the cathode.

### Conclusions

- The formation of intermediate, oxygen containing species with high melting points precludes the use of temperatures relatively close (less than 1750°C) to the melting point of pure titanium to electrowin molten titanium from titanium dioxide.
- Thermal convection and the high reactivity between carbon and titanium oxides at high temperature precludes the use of carbon anodes in a molten titanium electrowinning process when operating the electrochemical cells at relatively low voltages where an electric arc is not formed.
- The use of an arc to make electric contact at the cell anode seems possible, but the penalty would be a significant loss in energy efficiency.

### Acknowledgements

This project was sponsored by the Innovation Fund and was undertaken in partnership with Mintek, the University of Pretoria and Risimati Engineers. Kumba Resources and BHP Billiton also supported the project.

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