Enrichment of Titanium Subchlorides in Molten Salts

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Current Status of Research on Titanium Smelting

Direct reduction processes of Ti oxide (TiO_2)

- FFC: **Electrochemical** reduction in molten $CaCl_2$
- OS: **Calciothermic** reduction in molten $CaCl_2$
- EMR/MSE: Reduction of in molten $CaCl_2$ by **electronically mediated reaction**
- PRP: Reduction of TiO_2 preform by **Ca vapor**

Difficulties in these processes

- Production of high-purity TiO_2 feed is expensive.
- Energy efficiency and production rate are low.
- Metal/salt separation is difficult.
- **Purity control of obtained Ti is difficult.**

Current Status of Research on Titanium Smelting

Ti smelting process based on chloride metallurgy

- Armstrong: **Sodiothermic** reduction of $TiCl_4$
- Ginatta: **Electrochemical** reduction of $TICl_4$
- Fuwa: **Magnesiothermic** reduction of $TiCl_2$

Advantages in these processes

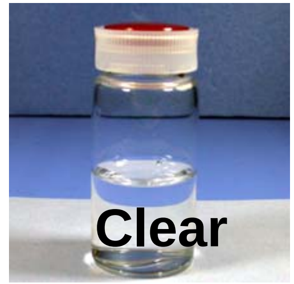
- Oxygen and iron removal by chlorination process is highly efficient.
- **High-purity Ti with low oxygen is available** by carrying out reduction process in oxygen-free system.

Ti smelting process based on magnesiothermic reduction of Ti subhalide

Subhalide Reduction Process

- **Continuous** and **high-speed** production
  Heat produced by reduction can be small.
  Heat extraction rate can be increased.
- **No iron contamination**
  Ti reaction container can be utilized.
- High purity Ti products with **low oxygen**

Physical and Chemical Properties of Titanium Chlorides

	$TiCl_4$	$TiCl_3$	$TiCl_2$
Appearance			
Color	**Clear**	**Red**	**Black**
Molecular weight (g/mol)	189.7	154.2	118.8
Density (g/cm^3)	1.70	No data	3.13
Melting point (°C)	–24.1	–	–
Boiling point (°C)	136.5	–	–
Sublimation point (°C)	–	830	1307
ΔG°_f at 800°C (kJ/mol Cl_2)	–317	–327	–344
$\Delta G'^\circ_f$ at 800°C (kJ/mol Ti)	–637	–491	–344
Vapor pressure at 800°C (atm)	–	0.74	1.2×10^{-4}

Reduction of Titanium Subchlorides

- Low reduction heat

At 1073 K

① $TiCl_4(g) + Mg(l) \rightarrow TiCl_2(s) + MgCl_2(l)$

$\Delta H^\circ = -339$ kJ, $\Delta G^\circ = -185$kJ

Suitable for developing high speed process

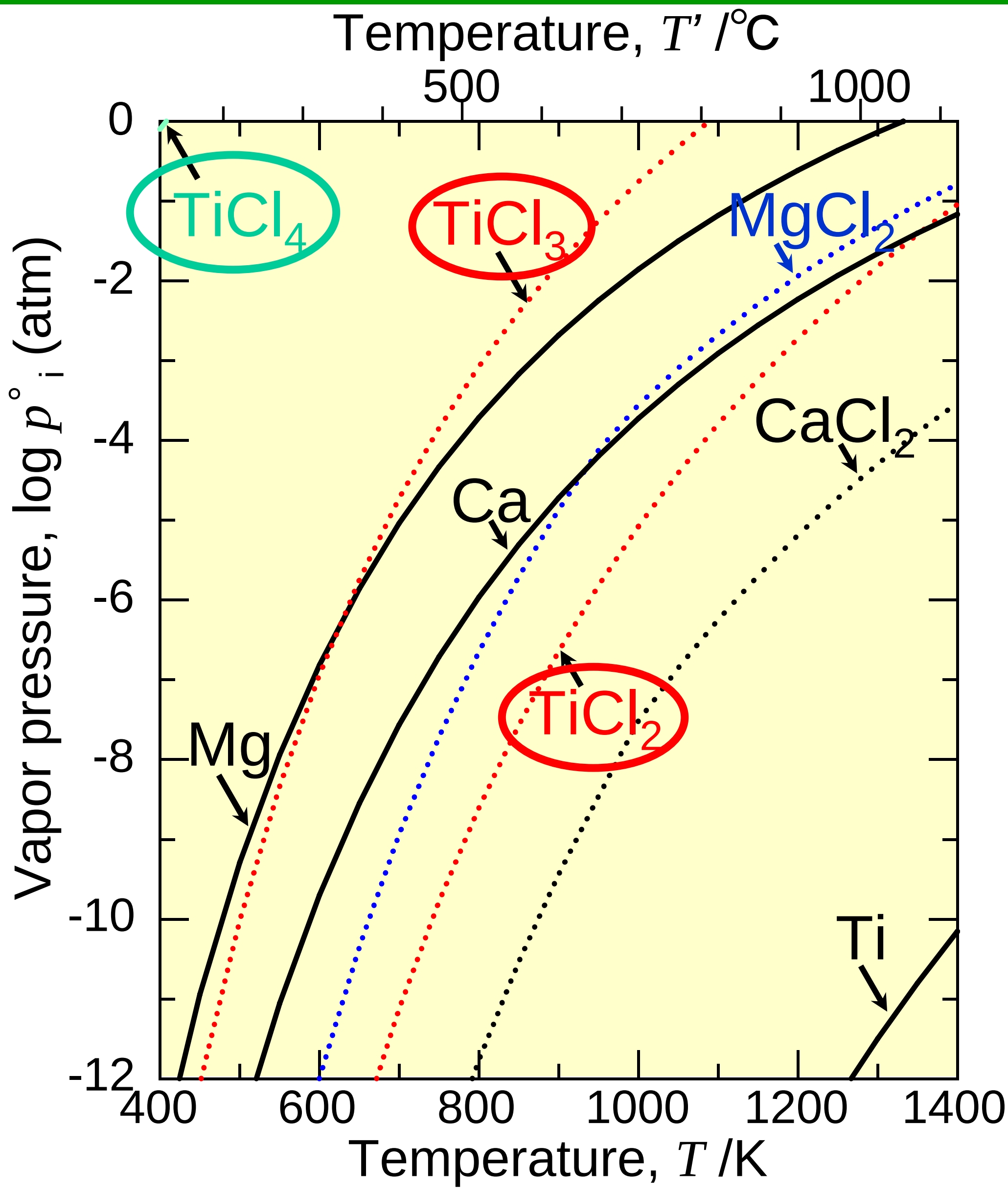
② $TiCl_2(s) + Mg(l) \rightarrow Ti(s) + MgCl_2(l)$

$\Delta H^\circ = -91$ kJ, $\Delta G^\circ = -130$ kJ

③ $TiCl_4(g) + 2\ Mg(l) \rightarrow Ti(s) + 2\ MgCl_2(l)$

(=①+②) $\Delta H^\circ = -430$ kJ, $\Delta G^\circ = -315$ kJ

Vapor Pressure of Titanium Subchlorides



- Low vapor pressure
- Stable as condensed phase

Density of reaction field and heat extraction rate drastically increase.

[I. Barin, Thermochemical Data of Pure Substances, VCH Verlagsgesellschaft, Weinheim, (1989).]

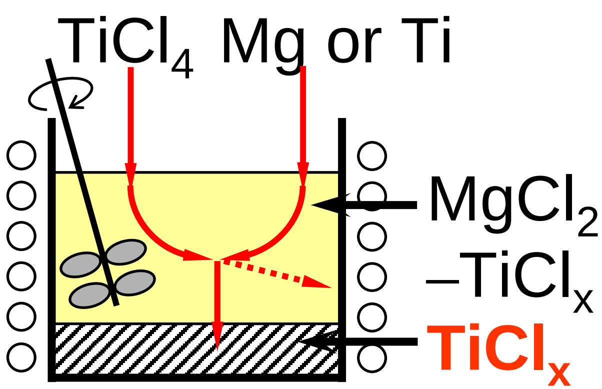
New Titanium Production Process Using Titanium Chlorides

① $TiCl_4(l, g) + Mg(l, g) \rightarrow TiCl_x(s, l) + MgCl_2(l)$

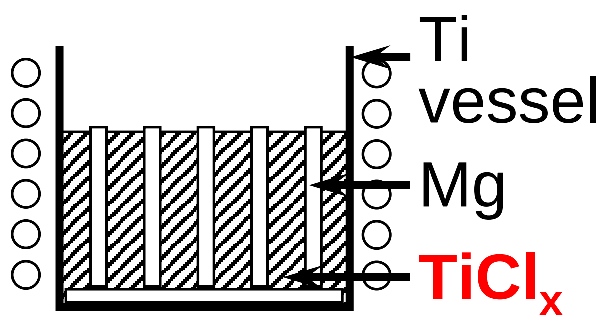
$TiCl_4(l, g) + Ti(s, \text{scrap}) \rightarrow TiCl_x(s, l)$

② $TiCl_x(s, l) + Mg\,(l, g) \rightarrow Ti\,(s) + MgCl_2\,(l, g)$

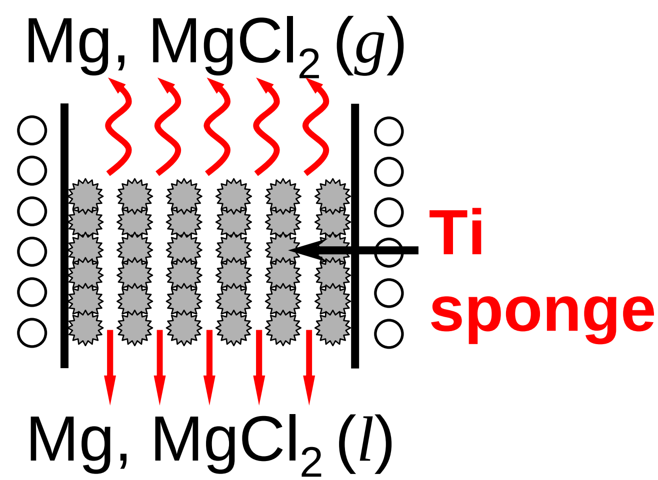
Step 1:
Production of
Ti subchlorides and
enrichment of $TiCl_x$



Step 2:
Magnesiothermic
reduction of $TiCl_x$



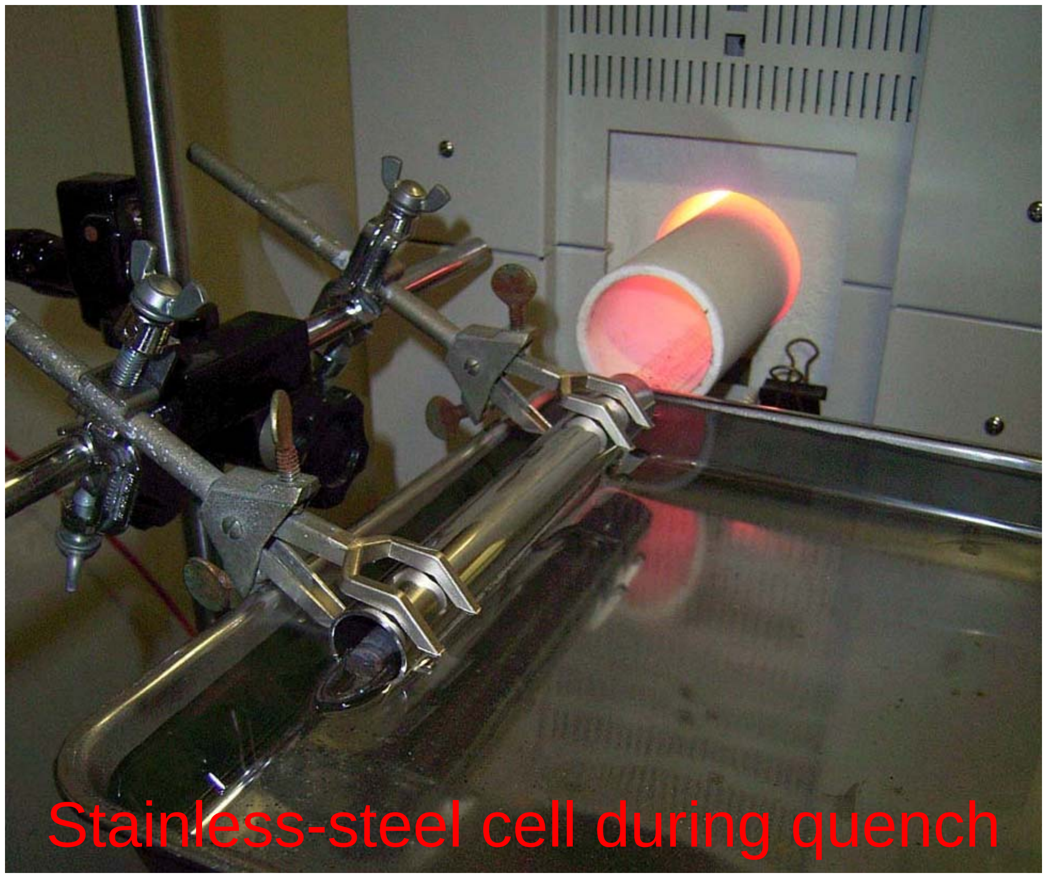
Step 3:
Removal of Mg and
$MgCl_2$ from Ti sponge
by draining and
vacuum distillation



Features of the Subhalide Reduction Process

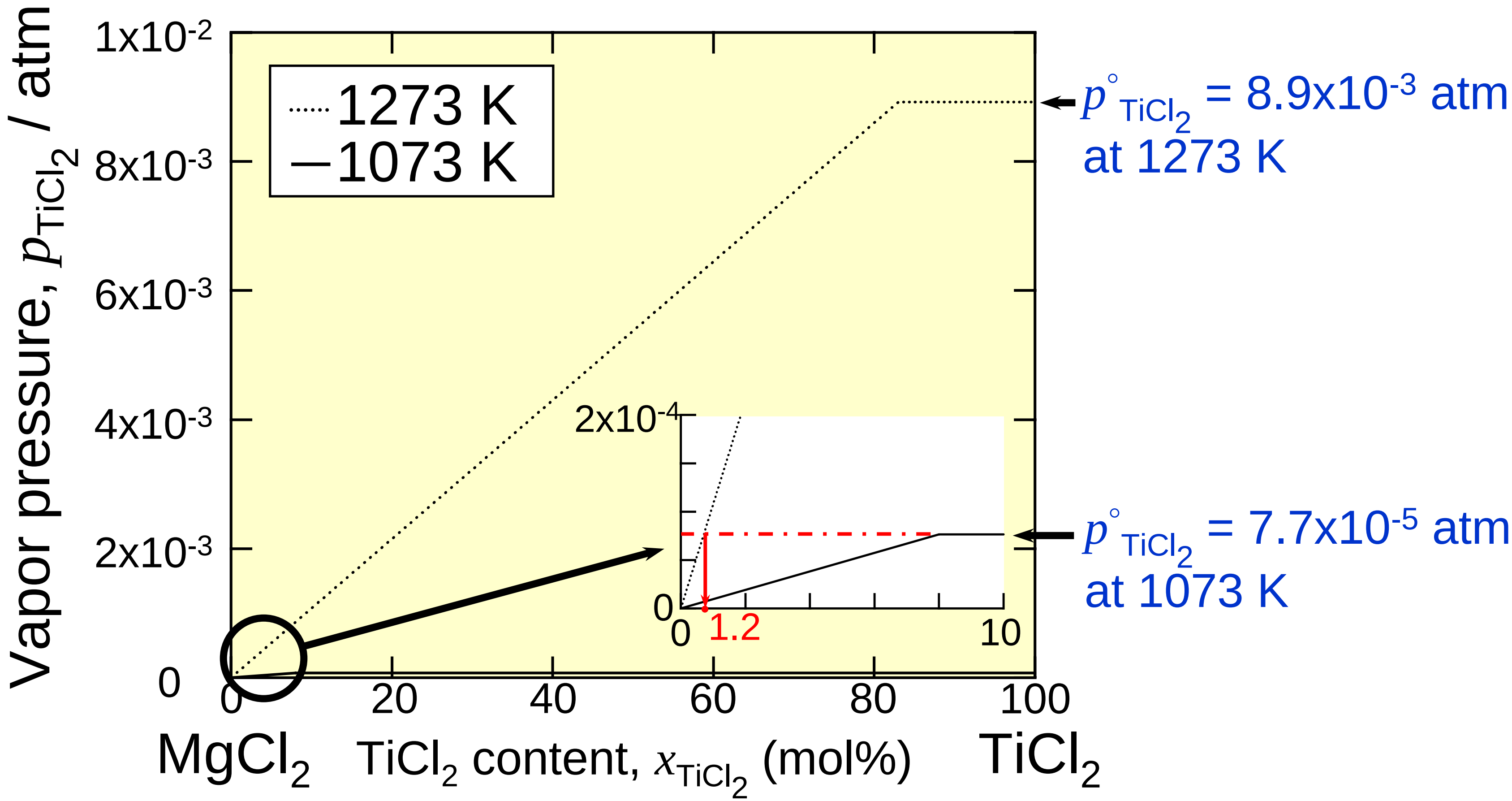
	Kroll process	Subhalide Reduction process
Process type	Batch-type, limited speed	(Semi-)Continuous, high speed
Feed material	$TiCl_4$ (*l*, *g*)	$TiCl_2$ or $TiCl_3$ (*s*, *l*)
Heat of reduction, ΔH° / kJ mol Ti	High (–434)	Low (–94 ~ –191)
Reactor material	Mild steel (Fe contamination unavoidable)	Ti (No Fe contamination)
Reactor size	Large (Crush and melt)	Small (No crush and direct melt)
Flux, sealant	Not used	$MgCl_2$, Ti
Common features	• Magnesiothermic reduction of chloride • Removal of $MgCl_2$ and Mg from Ti sponge by draining and vacuum distillation • Production of high-purity Ti with low oxygen content	

Enrichment of $TiCl_x$ in Molten Salts



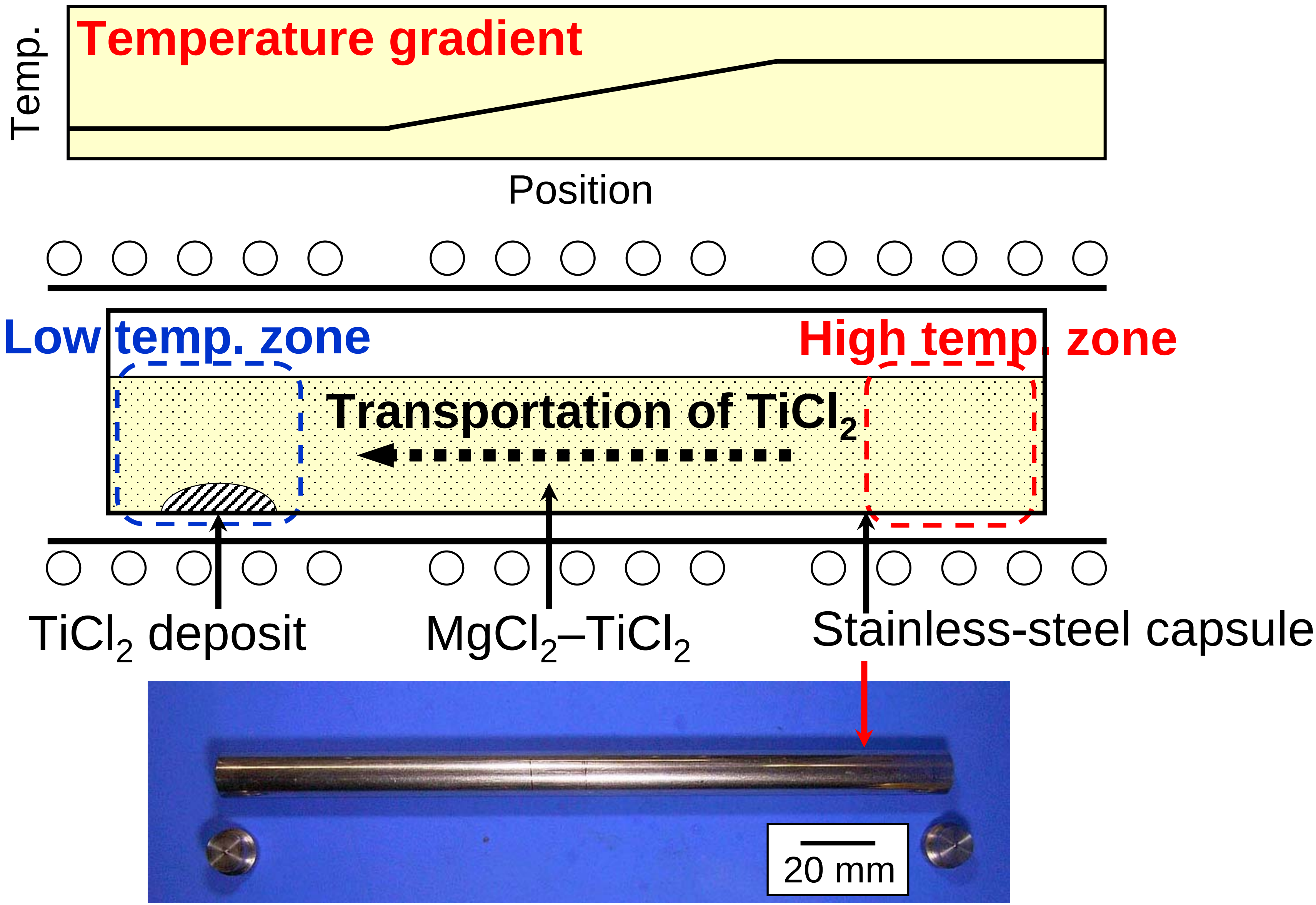
Enrichment of $TiCl_x$ in Molten Salt

$MgCl_2$–$TiCl_2$ quasi-binary system



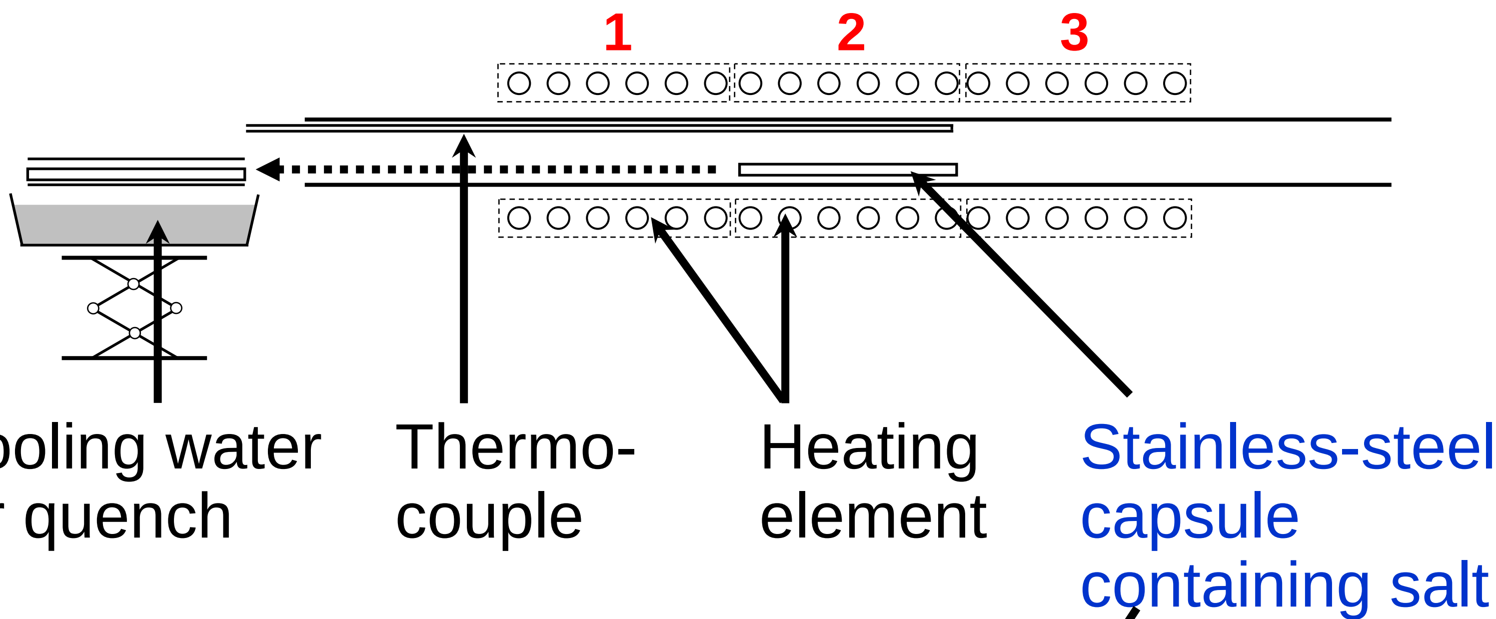
Utilization of temperature dependence in vapor pressure

Experimental Procedure



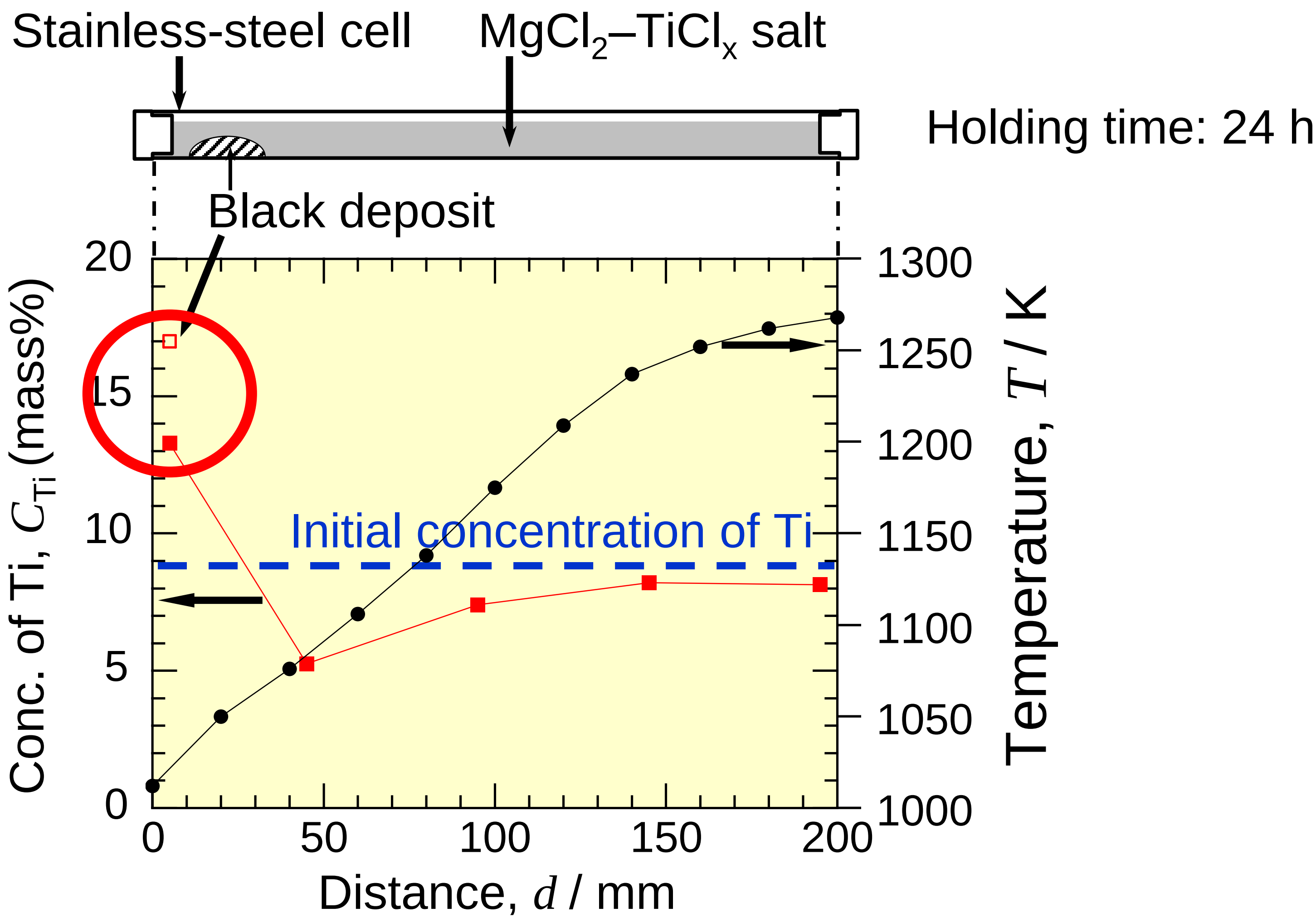
Experimental Procedure

3 zone furnace



Stainless-steel capsule

Experimental Results



Ti concentration at lower temperature part increased.

Conclusions

In order to establish a new semi-continuous and high-speed Ti production process based on magnesiothermic reduction of titanium subchlorides, a novel enrichment process of titanium subchlorides ($TiCl_x$, x = 2, 3) in molten salts was investigated.

- Feasibility of enrichment process for $TiCl_x$ in molten $MgCl_2$ was demonstrated.