NEW TITANIUM PRODUCTION PROCESS BY MAGNESIOTHERMIC REDUCTION OF TITANIUM SUBHALIDES

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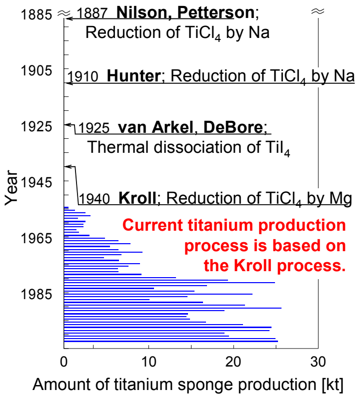
Introduction

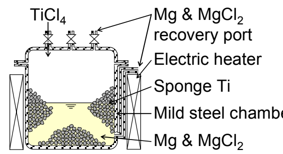
History of titanium metallurgy and production of titanium sponge in Japan

1791 **Gregor**; Discovery of titanium element

1795 **Klaproth**; Denominated as "Titanium"



The Kroll process



Chlorination: $TiO_2 + C + 2\,Cl_2 \rightarrow TiCl_4 + CO_2$

Reduction: $TiCl_4 + 2\,Mg \rightarrow Ti + 2\,MgCl_2$

Electrolysis: $MgCl_2 \rightarrow Mg + Cl_2$

Feature

◎**High purity titanium available**

◎**Effective metal / salt separation**

○Established chlorine circulation

○Utilizes efficient Mg electrolysis

○Reduction and electrolysis operation can be carried out independently

×Complicated process

×**Slow production speed**

×**Batch type process**

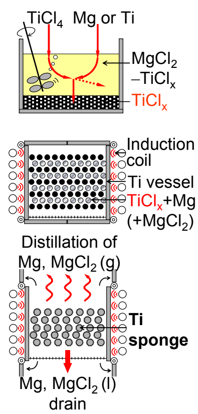
Kroll process is huge exothermic reaction →It requires several days to produce titanium in large (ton) scale.

New titanium production process using titanium subhalides ($TiCl_x$, x=2, 3)

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

$TiCl_4$(l, g) + Ti (s, scrap) → $TiCl_x$ (s, l)

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



Step 1: High speed production of Ti sub-chlorides, and enrichment of $TiCl_x$

Step 2: High speed magnesiothermic reduction of $TiCl_x$

Step 3: High speed removal of Mg and $MgCl_2$ from Ti sponge by drain and vacuum distillation

Comparison of the Kroll process and new process

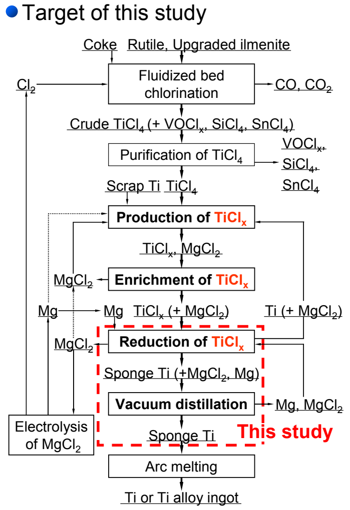
	Kroll process	This study
Process type	Batch, low speed	(Semi-)Continuous, high speed
Feed material	$TiCl_4$ (l, g)	$TiCl_2$ or $TiCl_3$ (s, l)
Heat of reduction, $\Delta H°$ / kJ molTi	– 434 (Huge heat)	– 94 ~ – 191 (Small heat)
Reactor material	Mild steel (Iron contamination unavoidable)	Titanium (No iron contamination)
Reactor size	Large (Crush and melt)	Small (No crush and direct melt)
Flux, sealant	No use	$MgCl_2$, Ti
Common features	Magnesiothermic reduction of chloride. Removal of $MgCl_2$ and Mg from Ti sponge by draining and vacuum distillation. Ti with low oxygen is produced.	

Purpose of this study:

Establishment of continuous and high speed titanium reduction process based on magnesiothermic reduction of titanium sub-chlorides.

Experimental

Target of this study



Magnesiothermic reduction of $TiCl_3$ and removal of by-product by vacuum distillation

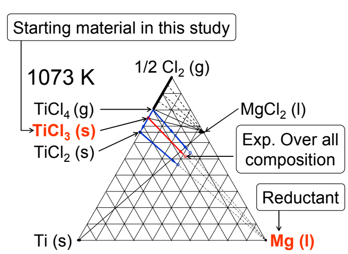


Fig. Phase diagram for the Ti-Mg-Cl system at 1073 K. (Ref. Okabe et al.: J. Japan Inst. Metals 61 (1997) pp. 610-618.)

Procedure: $TiCl_3$ and Mg set into a titanium vessel were heated in Ar atmosphere, and the temperature change by magnesiothermic reduction of $TiCl_3$ was monitored. After the reduction, excess Mg and by-product $MgCl_2$ were removed by draining and vacuum distillation.

Experimental apparatus

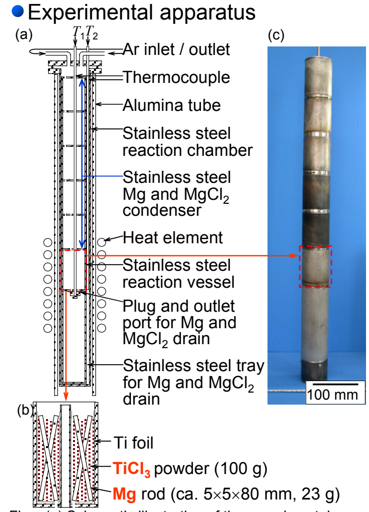
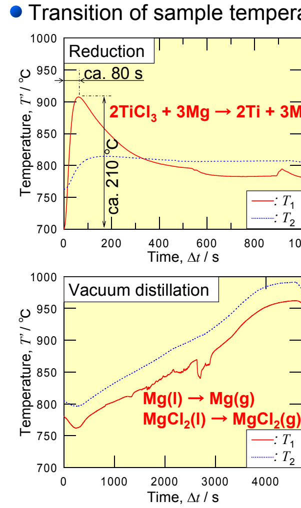


Fig. (a) Schematic illustration of the experimental apparatus for magnesiothermic reduction of $TiCl_3$, (b) inner setup of reaction vessel, (c) vessel arrangement.

Transition of sample temperature



Magnesiothermic reduction of $TiCl_3$ proceeded at high speed.

Results

Appearance of obtained samples

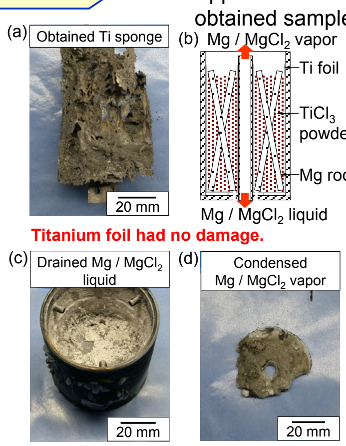


Fig. (a) Photograph of obtained Ti sponge after magnesiothermic reduction of $TiCl_3$, (b) schematic illustration of experimental setup, (c) photograph of drained $MgCl_2$ and Mg liquid, (d) condensed $MgCl_2$ and Mg vapor.

Analytical results

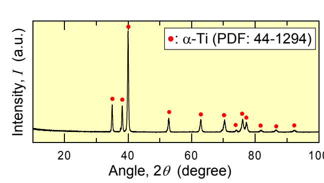


Fig. XRD pattern of the obtained Ti sponge (Cu-Kα).

Table Analytical results of the obtained Ti sponge after magnesiothermic reduction of $TiCl_3$.

Concentration of element i, C_i (mass%)[a, b]						Yield
Ti	Fe	Ni	Cr	Mg	Al	(%)
99.18	0.50	0.01	0.02	0.09	0.21	87

a: Determined by X-ray fluorescence analysis, and the value excludes carbon and gaseous elements.

b: This value is average of the samples obtained from top and bottom part of Ti sponge.

・Pure metallic titanium was obtained by this process.

・Pathway for supplying Mg reductant to feed $TiCl_3$ was found to be important from various experiments.

Control experiment for evaluation of iron contamination from crucible

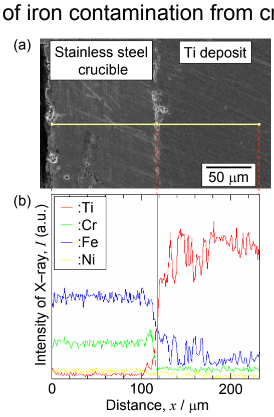


Fig. (a) SEM image of sectioned crucible after reduction experiment, (b) element concentration profile across the boundary between stainless steel crucible and Ti deposit.

Iron contamination from stainless steel crucible is unavoidable.

Conclusion

New titanium production process based on magnesiothermic reduction of titanium subhalides was proposed, and its feasibility was demonstrated. In detail…

・High speed magnesiothermic reduction of $TiCl_3$ was carried out, and possibility for developing high speed reduction process was demonstrated.

・Pathway for supplying Mg reductant to $TiCl_3$ feed was found to be important.

・Ti crucible was shown to be applicable to magnesiothermic reduction of $TiCl_3$, and new anti-contamination process was proposed.

Currently, we are developing advanced processes (eg. $TiCl_2$ production) for new titanium production process.

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