Ceramic Membrane in Direct Reduction of TiO_2 in Molten $CaCl_2$

N.Asahara, M.Yoshida, Y.Matsuoka and R.O.Suzuki
Graduate School of Energy Science, Kyoto Univ.,
Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501 Japan

Calciothermic reduction for Ti metal production has been proposed that TiO_2 instead of $TiCl_4$ is used as the starting materials [1]. The molten $CaCl_2$ is the solvent of both Ca and the byproduct CaO. The reduction of TiO_2 and the electrolysis of CaO are conducted in a single bath; a few mol%Ca in the salt produces a strong reducing atmosphere that reduces TiO_2 thermochemically. CaO is electrolyzed into Ca and CO/CO_2 gases when carbon is used as the anode. However, carbon often pollutes the product Ti. The purpose of this work is to study the mechanism of carbon contamination in this process, and to show the effect of ceramic membrane isolating the evolved gases from the Ti powder, as shown in Fig.1.

Ti powder immersed in the $CaCl_2$ was exposed to the CO_2 gas injected into the melt. The raw powder (70 mass ppm carbon) was contaminated to 1800 ppm carbon at 1173K for 7.2 ks in the flow rate of 2L/min. When MgO membrane was arranged between TiO_2 and the gas nozzle, the C content in Ti decreased to 630 ppm carbon in the same severe condition.

As shown in Fig.2, this porous MgO membrane was arranged between TiO_2 and the carbon anode. When the electrolysis was conducted at 5V at 1173K for 7.2ks, the current decreased by about 1/2 (in case Fig.2(a)) and 1/8 (in case Fig.2(b)), in comparison with that when porous MgO crucible was not used. As shown in Table 1, the C contents in Ti were successfully lowered with MgO membrane in both cases when the same amount of electricity was applied. These values are less than 300 ppm C, defined in the industrial standard for pure Ti.

ZrO_2 membrane was applied, as shown in Fig.1 (B), the CO and CO_2 gases are completely separated from the Ti and the molten salt, although O^{2-} can transmit through this solid ionic conductor. α -Ti was obtained when the total charge of 15000C was applied at 1173K for 54.0ks (Fig.3.).

[1] R.O.Suzuki, K.Teranuma and K.Ono, Metall. Mater. Trans. B., vol. 34B, pp. 287-295, (2003)

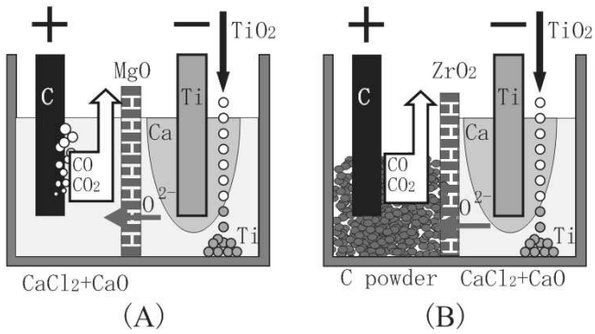

Fig.1. Ti reduction process with ceramic membrane.

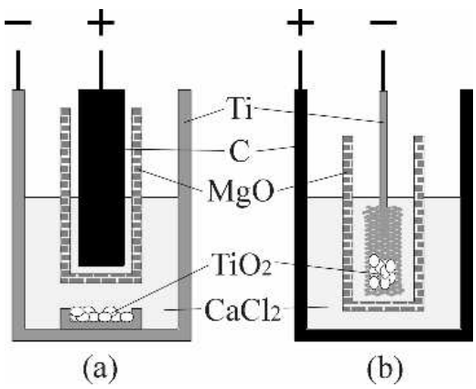

Fig.2. Experimental arrangement.

Table 1 Carbon and oxygen content.

arrangement	(a)	(b)
without membrane	0.47%C	0.30%C
	4.5%O	2.4%O
with membrane	0.019%C	0.021%C
	2.7%O	4.3%O

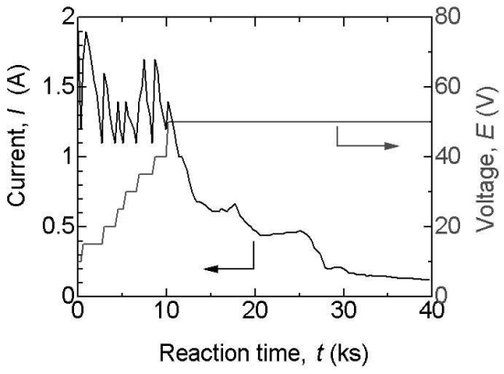

Fig.3. Current and voltage during electrolysis using ZrO_2 membrane