REDUCTION OF TITANIUM DIOXIDE BY CALCIUM IN HOT CATHODE SPOT

TAKEO OKI and HIROSHI INOUE

Department of Metallugical Engineering

(Recieved May 31, 1967)

Synopsis

Reduction of titanium dioxide by calcium produced in hot cathode spot was investigated in fused salt (liq-$CaCl_2$).

In cathode in fused $CaCl_2$ salt, titanium dioxide was simultaneously reducted by calcium produced by electrolysis of the same $CaCl_2$ salt.

TiO_2 was changed successively as follows: $TiO_2 \rightarrow Ti_2O_3$ and $CaTiO_3 \rightarrow Ti$. CaO produced in this reduction reaction was impeding so-called anode effect successfully.

1. Introduction

Reduction of titanium dioxide powder in cathode by active calcium, being electrodeposited simultaneously in electrolysis of the same bath, in hot cathode spot, was investigated. In this experiment calcium is a very excellent reductant among some metals and the hot cathode spot is also a good reaction place, which is obtained by concentration of electric current into smaller cathode and of which temperature is raised so higher. Then reductant calcium is obtained simultaneously by electrolysis of fused $CaCl_2$ salt. The calcium produced reacts immediately with titanium dioxide in the same cathode as follows and finally titanium is obtained, it is expected.

TiO_2 (in cathode)+Ca (produced in same cathode)
=Ti+CaO (dissolved into $CaCl_2$ fused salts) (1100–1800°K)
$\Delta G_T^\circ = -88{,}642+9.45\ T$

The results in some experiments for this process are reported and the possibility of this process is also discussed.

2. Experimental

2.1 Experimental apparatus and materials

Experimental apparatus is shown in Fig. 1. TiO_2 is rutile type powder and is chemically pure. $CaCl_2$ is of reagent grade and dehydrated by pre-fusion.

2.2 Experimental procedure

Put sample TiO_2 (ac. 30 gr in this experiment) with cathode electrode into alumina crucible, and put the alumina crucible into large graphite crucible and put $CaCl_2$ (dehydrated and crushed) into the graphite crucible. Then by heating, temperature of specimen is reached to specified temperature.

Then start electrolysis and do during the specified hours under specified con-

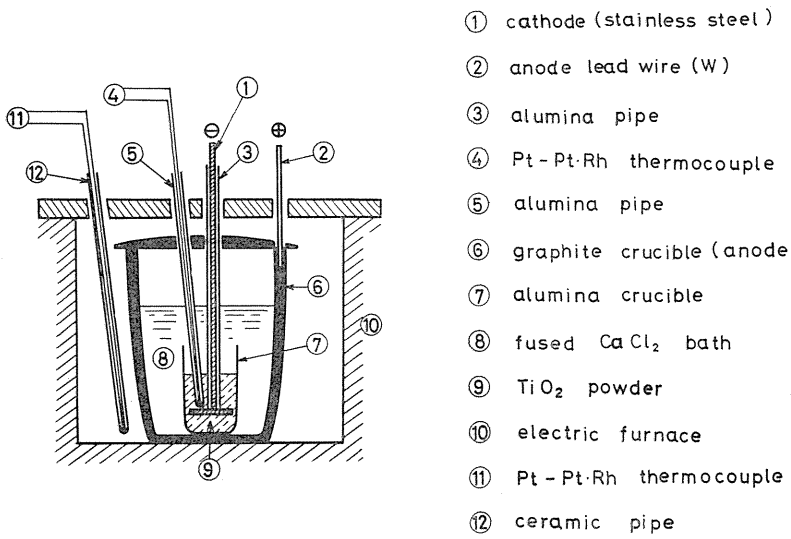

FIG. 1. Experimental apparatus.

stant conditions. After electrolysis, put out the alumina crucible with electrode, and leach it with dil-HCl and water-wash it. The sample produced is offered for weighing, X-ray analysis, chemical analysis etc.

3. Experimental results and consideration

Experimental results for Ca reduction of TiO_2 in hot cathode spot in fused salts are shown in Table 1.

It is of course observed that the higher current density of cathode is, the higher the temperature at the cathode spot is. Table 1 shows that the higher the reaction temperature (cathode spot temperature) is, the better the reduction

TABLE 1. Experimental results for Ca reduction of TiO_2 in hot cathode spot

Bath temp., °C	Reaction hr., min	Hot spot temp., °C	X-ray analysis of product
830	30	1145	Ti, $CaTiO_3$
820	10	1120	Ti_2O_3, $CaTiO_3$
850	5	1220	TiO_2, Ti_2O_3, $CaTiO_3$
860	3	1060	TiO_2, $CaTiO_3$
850	1	1010	TiO_2
840	5	900	TiO_2, $CaTiO_3$
1040	5	1085	$CaTiO_3$
830	30	1145	Ti, $CaTiO_3$
850	30	900	$CaTiO_3$
960	30	1060	$CaTiO_3$
954	60	1040	Ti, $CaTiO_3$
940	120	1118	Ti, $CaTiO_3$
950	30	1500	Ti
960	30	1300	Ti

reaction ocurrs, and the longer the reaction hour is, the better the procedure degree of the reaction is. Then at bath temperature of 950°C, and at hot spot temperature of 1300–1500°C the best results of reduction are obtained, *i.e.* only titanium is produced at hot cathode spot.

Now we shall have some consideration. The reaction mechanism in reduction of titanium dioxide by calcium produced in hot cathode spot in fused $CaCl_2$ salts is considered as follows, on the basis of X-ray analysis.

$$3\,TiO_2+Ca \rightleftarrows CaTiO_3+Ti_2O_3 \qquad \cdots\cdots \text{1st stage}$$

$$\left(\text{or } \begin{array}{l} 2\,TiO_2+Ca \rightleftarrows Ti_2O_3+CaO \\ TiO_2+CaO=CaTiO_3 \end{array}\right)$$

$$\left.\begin{array}{l} Ti_2O_3+3\,Ca=2\,Ti+3\,CaO \\ \left(\text{or } \begin{array}{l} Ti_2O_3+Ca=CaO+2\,TiO \\ TiO+Ca=Ti+CaO \end{array}\right) \\ CaTiO_3+2\,Ca=Ti+3\,CaO \end{array}\right\} \qquad \cdots\cdots \text{2nd stage}$$

CaO produced in the 2nd stage reaction is dissolved into $CaCl_2$ fused salts and so is preventing so-called anode effect in graphite anode, we think.

Titanium produced at optimum conditions in this experiment has about 8 percent calcium, but after vacuum distillation, the ca-distilled Ti has good purity (a.c. 98–99%).

In case of including of some $CaTiO_3$ into Ti, separation of Ti from $CaTiO_3$ is very difficult, so the experimental condition must be selected not to leave the $CaTiO_3$ in Ti. For that, the temperature has to be elevated as higher as possible by controlling the current density of hot cathode spot. And the reaction hours have to be taken enough to end the reduction reaction into Ti.

4. Conclusion

1) By reduction of titanium dioxide by calcium produced in hot cathode spot in fused $CaCl_2$ salt, titanium is produced, having about 8% calcium.

2) Reaction mechanism of this reaction is as follows (determined by X-ray analysis etc.)

$$TiO_2 \rightarrow CaTiO_2,\ Ti_2O_3(\text{suboxide}) \rightarrow Ti$$

3) CaO produced is dissolvled into fused salt and prevents the so-called anode effect.

We thank for Mr T. Hada's zealous co-operation in this experiment.