1. Direct Production of Ti-29Nb-13Ta-4.6Zr Biomedical Alloy

Applying the principle of the OS process[1,2], as illustrated in Figure 1, the electrolysis and the calciothermic co-reduction of an oxide mixture consisting of TiO$_2$, Nb$_2$O$_5$, Ta$_2$O$_5$, and ZrO$_2$ were combined to produce Ti-29Nb-23Ta-4.6Zr (TNTZ alloy) [3].

$$\text{TiO}_2 + \text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5 + \text{ZrO}_2 + \text{Ca} \rightarrow \text{TNTZ} + \text{CaO}$$

The by-product CaO dissolves into the CaCl$_2$ melt near the cathode. It is decomposed to metallic Ca and O$^2-$ . The latter is removed from the molten bath as CO and CO$_2$ gas at the anode. The precipitated Ca on the cathode also dissolves in the CaCl$_2$ bulk and reacts with the oxides as the reductant.

Fig. 1 Principle of OS process for alloy formation.

![Principle of OS process for alloy formation.](image1)

Fig. 2 Change in oxygen concentration versus supplied charge[3].

![Change in oxygen concentration versus supplied charge.](image2)
TNTZ alloy is a newly developed alloy that is used for biomedical purposes, and it is expected to find wide-ranging applications because of its advantageous properties [4,5]. Its constituent elements, namely, Ti, Nb, Ta, and Zr, are non-toxic to biological bodies. In addition, it has a low Young’s modulus of 60 GPa—similar to that of cortical bones—and its mechanical strength is similar to that of Ti-6Al-4V alloy.

Ca was produced by the electrolysis of CaO in molten CaCl₂ by applying a voltage of 3.2 V between a carbon anode and Ti cathode at 1173 K. The powdery oxide mixture without sintering was filled in the basket-like cathode and immersed into the molten salt. The current during electrolysis exhibited a comparatively large value at the initial stage; it then gradually decreased, and approached a low and constant value.

The oxygen concentration residual in the obtained powder decreased monotonically with an increase in the supplied electric charge, \( Q \), as shown in Figure 2. \( Q_0 \) is defined as the electric charge necessary to generate the required amount of Ca stoichiometrical for equation (1). An oxygen concentration of 0.19 mass% was attained by supplying the electrical charge around three times larger than \( Q_0 \).

Figure 3 shows the phase identifications by X-ray diffraction measurements, where \( \alpha \) and \( \beta \) correspond to HCP and BCC solid solutions, respectively. \( \alpha \) and \( \beta \) phases were generated effectively during electrolysis. However, TiO₂ and ZrO₂ would react with CaO dissolved in the molten salt to form the complex oxides such as CaTiO₃ and CaZrO₃. This implies that the reduction behavior (reduction rate) could be classified into two groups, based on the free energy change in the chemical reaction (oxygen removal from the oxide): a group of Ta and Nb and another of Ti and Zr. The elements in the latter group are thermodynamically more stable than those in the former one. The elements in the former and the latter group consist of BCC \( \beta \)-phase and HCP \( \alpha \)-phase, respectively. When the electric charge reached 165% of \( Q_0 \), only the \( \alpha \) and \( \beta \) phase were found. The smaller intensity of the \( \alpha \) peak indicated the transformation of \( \alpha \) to \( \beta \). At 323%, TiC precipitation was observed. This is due to the generation of carbon via the reduction of CO and CO₂ as a parasite reaction. At all stages, a residual \( \alpha \) phase was detected; in contrast, it was reported that the arc-melted TNTZ alloy had a \( \beta \) single phase.

Fig.3  XRD patterns of reduced samples [3].
At \( Q/Q_0 = 262\% \) (Figure 4), the distribution of the four elements was measured by SEM and EDX. The homogeneous distribution of them for a wide area was found, but the measured compositions at eight locations exhibited slight variations. A residual \( \alpha \) phase probably exists due to differences in the reduction behavior of the constituent oxides. The differences in the reduction rate lead to variations in the elements. This is because the initial product Nb and Ta metals form the blocks in precipitation morphology, whereas the delayed product Ti and Zr cannot diffuse well in the blocks in a few tens \( \mu \)m. Zr acts as an HCP stabilizing element in Ti alloy, whereas Nb and Ta act as BCC stabilizing elements. Therefore, the variability of elements causes the residual \( \alpha \) phase (HCP).

Several reduced samples in metallic state were sintered for future application in powder metallurgy. They were pressed into the pellet (diameter: 10mm, thickness: of the order of a few millimeters) at 450 MPa and then sintered in Ar atmosphere. After sintering at 1300 K for 54 ks, for example, the Ti- and Zr-rich HCP phase disappeared and the composition achieved the homogeneous targeted value, as shown in Figure 5.

The results of this study indicate that the OS process can be applied to directly produce TNTZ alloy from an oxide mixture, although the standard free energy of oxide formation is largely different in the starting oxides. The way from the oxide mixture to metallic alloy was not well studied in case of Ti-V-Cr [6] and Ti-Al-V [7] alloys, but this work shows the importance of thermodynamically (=electrochemically) stepwise reactions. The preferential reduction for \( \text{Nb}_2\text{O}_5 \) and \( \text{Ta}_2\text{O}_5 \) should be minimized and the metallic mixture can be homogenized by sintering.

![Fig. 4 SEM image and elemental concentration mappings of the sample obtained at \( Q/Q_0 = 262 \% \).](image)

The time dependency of current was inserted for this sample [3].
2. Reduction of TiO and CaTiO$_3$ in Molten CaCl$_2$

In the reduction path from pure TiO$_2$ to metallic titanium by using the electrolysis in the molten CaCl$_2$, several lower oxides often formed; such as Ti$_3$O$_5$ in the Ti-O binary system. Because the by-product CaO reacts with the residual TiO$_2$ easily even in the molten media such as CaCl$_2$, the formation of intermediate phase of CaTiO$_3$ was also often reported in the previous studies. However, the appearance of TiO phase has never reported. It is considered that the first product from TiO$_2$ is CaTiO$_3$ and it is subsequently reduced to metallic Ti via Ti$_3$O$_5$, Ti$_2$O, and TiO, and not through TiO.

TiO is a stable oxide in the Ti-O binary system, and the reduction of monoxide TiO to Ti does not occur even if a strong reactant such as carbon is applied to TiO$_2$. In the other words, TiO is practically a final product of carbon reduction from TiO$_2$, and the oxygen removal from TiO is economically desired to obtain the metallic Ti. Applying the principle of the OS process, the electrolysis and the calciothermic reduction of TiO was studied in addition to TiO$_2$ and CaTiO$_3$. Zhu et al. reported the dissolution and precipitation of Ti from the TiO anode in the molten chloride [8], while we examined the cathodic reaction of TiO in the molten salt.

In order to confirm the strong reducing ability of Ca thermodynamically, the calciothermic reduction in the molten CaCl$_2$ was firstly applied to either TiO powder (sieved under 300 mesh) or the arc-melted and densely solidified TiO lumps. The TiO sample was encapsulated in the stainless steel vessel with the metallic Ca lumps and CaCl$_2$, and heated in Ar gas at 1173K for 30 min. The application of OS process to TiO powder or lumps was also conducted using the MgO crucible filled with about 660g of 0.5mol%CaO+CaCl$_2$.

The Ti powder containing about 2 mass % oxygen could be obtained by the calciothermic reduction, i.e., without any electrolysis. The oxygen concentration change during the electrolysis is shown in Figure 6. The same Ti basket as the cathode and the graphite straight bar as the anode were commonly used for TiO$_2$, CaTiO$_3$ and TiO powder (<300 mesh). Even when 10 times larger amount of electricity $Q$ than $Q_0$ was given, the oxygen concentration did not drop to the level below 6 mass% in case of TiO starting. Previously Kar and Evans [9] predicted from the calculation that TiO could enhance the reaction and the CaTiO$_3$ formation might disturb the deoxidation, but their assumptions should be revised to apply their models to OS process.
**Figure 7** shows the isothermal section of Ti-Ca-O ternary phase diagram at the reduction temperature. It is deduced from the Ti-O, Ti-Ca, Ca-O and TiO₂-CaO binary diagrams, from the standard free energy for formation of compounds and also from the experimental phase identifications on the partially reduced samples when TiO₂ and CaTiO₃ were chosen as the starting material. Several oxides existing at the compositional line between TiO₂ and TiO were not found in the experiments, and skipped in this figure. In case of reduction from TiO, any compound containing Ca was not detected, while the reduction either from TiO₂ or CaTiO₃ formed CaTi₂O₄ as the intermediate compound to metallic Ti. The three phase combination, for example, CaTi₂O₄-CaTiO₃-α-Ti, was also confirmed in the Ar gas atmosphere, by sintering TiO, CaTiO₃ and Ti.

**Figure 8** shows the SEM image of the TiO bulk sample after the calciothermic reduction. Only the surface
layer was reduced to $\alpha$-Ti and the internal part remained as the unreacted TiO. It shows the coexistence as the ternary equilibrium among Ca, Ti, and TiO in the molten CaCl$_2$. Although some small cracks and pores could be found in the layer, it is relatively dense and adhered tightly to the unreacted TiO core. In the bulk CaTiO$_3$, such a layer was rarely found and all the partially reduced samples were easily broken into pieces.

![Diagram of TiO layer](image)

**Fig.8** Cross-sectional view of TiO after the electrolysis for 13 ks at 1173 K and 3.1V.

These findings suggest that the oxygen diffusion in the Ti layer and/or TiO bulk becomes the rate determining step, and that the formation of TiO on the way from TiO$_2$ starting material becomes obstacle to remove oxygen from the sample. When TiO happens to be formed, the Ti thick layer on TiO particle makes the reaction slower.

On the other hand, the formation of CaTiO$_3$ slightly delays the reduction and deoxidation (oxygen removal), when compared with the reduction from TiO$_2$, as shown in Figure 6. The higher concentration of CaO near the oxide particles and a slight sintering of CaTiO$_3$ might delay the oxygen diffusion from the oxide to the CaCl$_2$ bulk. However, the weak mechanical strength and the pulverizing nature of CaTiO$_3$ phase during oxygen loss assists to keep the wider diffusion path of Ca and CaO.

Therefore, the formation of CaTiO$_3$ enhances a sequence of oxide reduction, because it holds high porosity and paths for the salt penetration. Because the formation of CaTiO$_3$ was frequently reported and that of CaTi$_2$O$_4$ was rarely, the formation of CaTi$_2$O$_4$ may be non-rate-determining factor in the reduction sequence from TiO$_2$. As indicated in Figure 6, the reduction rate approximately looks similar for TiO$_2$ and CaTiO$_3$. In OS mechanism, CaTiO$_3$ is natural product between the residual TiO$_2$ and the by-product, and it may support the oxygen diffusion to the particle surface.

**3. Reduction of CO$_2$ gas**

Because the OS process could be applied to the reduction of oxide liquid such as V$_2$O$_5$ [10,11], we tried to expand the OS mechanism to the reduction of gaseous oxides such as CO$_2$ gas. The gas was introduced through the cathodic stainless steel pipe into the 0.5mol%CaO+CaCl$_2$ melt, as shown in Figure 9.

When the carbon anode was used for reduction of CO$_2$ gas, we can not identify the mechanism because O$^-$ turns to CO and CO$_2$ gas by contacting with C. Therefore, the oxygen conductive yttria stabilized ZrO$_2$ (YSZ) was used as the ceramic anode to remove O$^-$ from the melt.
Ca^{2+} + 2e \rightarrow \text{Ca(in CaCl}_2\text{)} \text{ at/near the cathode} \quad (2)

CO_2(g) + 2 \text{Ca(in CaCl}_2\text{)} \rightarrow \text{C(s)} + 2 \text{CaO} \text{ near the cathode} \quad (3)

CaO \rightarrow \text{Ca}^{2+} + \text{O}_2\text{-(in CaCl}_2\text{)} \text{ near the cathode} \quad (4)

2 \text{O}_2\text{-(in CaCl}_2\text{)} \rightarrow \text{O}_2(g) + 4e \text{ in the YSZ anode} \quad (5)

When the formed C were nano-tube or fullerene, it would be interesting for future applications. Both the precipitated carbon and the extracted oxygen gas can be used, for example, in the iron-making plants which exhaust a huge amount of CO_2.

**Figure 10** shows the results during the electrolysis for 20 hours at 1173K. The gas mixture of 9 vol%CO-9 vol%CO_2-82 vol%Ar, which imitates the exhaust gas from the blast furnace in iron making industry, was flown with the rate of 0.1L/min into the molten CaCl_2. At the initial stage a fairly large current was found, and the concentrations of CO and CO_2 dropped sharply. The decrease of gas concentration was closely related with the current. It suggests that the observed current is due to calciothermic reduction. At the later stage, the concentration of CO and CO_2 increased and decreased, respectively. This may be due to Boudouard reaction, where the precipitated carbon reacts with CO_2 to form CO gas. After the electrolysis the upper surface of the
melt was covered a black substance, which was identified by XRD and TEM observations as the aggregate of graphite fine particles as well as amorphous carbon, after well washed in water.

This CO$_2$ gas reduction can be explained well by OS mechanism on calciothermic reduction in CaCl$_2$ melt, as well as TiCl$_4$ gas reduction [12].

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