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Direct Production of Ti-29Nb-13Ta-4.6Zr Biomedical Alloy from Oxide Mixture in Molten CaCl₂

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Abstract

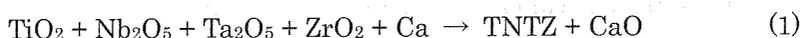
Ti-29Nb-13Ta-4.6Zr(TNTZ) alloy was successfully produced by co-reduction of oxide mixture, which consisted of TiO₂, Nb₂O₅, Ta₂O₅, and ZrO₂. This method uses high reduction capacity of deposited Ca or Ca-condensed molten salt. Ca was produced by controlled-potential electrolysis of CaO in molten CaCl₂ under 3.2V at 1173K with carbon anode and Ti cathode. Supplied charge Q was varied in the range of 0~400% of theoretical charge (Q_0) to generate the required amount of Ca to reduce the oxide mixture.

The oxygen concentration of the obtained powder sample decreased monotonously as the supplied charge increased. 1.37 mass% oxygen could be attained at $Q/Q_0=165\%$ and 1900 mass ppm at $Q/Q_0=323\%$. X-ray diffraction measurements identified the sample which has low oxygen concentration as the mixture of Ti-based BCC solid solution and a small amount of HCP solid solution. The electron probe microanalysis showed that the composition of this sample was slightly different from the targeted composition due to difference of reduction rate of the component oxides. After sintering at 1300K for 54ks, the HCP phase disappeared and the compositional homogeneity was improved within $\pm 3.5\text{mass}\%$ to the targeted composition.

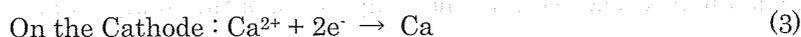
Introduction

TNTZ alloy is expected as new biomedical alloy because of its noble property of affinity to the biological bodies and low Young's modulus of 60 GPa, which is close to that of cortical bones. However, the manufacturing process of Ti-based alloy like TNTZ is still expensive and complex. The purpose of this work is to produce TNTZ alloy directly from oxide mixture of TiO_2 , Nb_2O_5 , Ta_2O_5 , and ZrO_2 by using a simple process.

Electrochemical process consists of calciothermic reduction and Ca recycling, so-called OS process, has been investigated[1]. This process uses high reduction capacity of deposited Ca or Ca-dissolved molten salt[2]. The calciothermic co-reduction of oxide mixture is expressed in total as,



The by-product CaO dissolves in molten CaCl_2 immediately, and is electrolyzed[3]. During the electrolysis, the oxygen is removed as CO and CO_2 gas at the carbon anode, and Ca is regenerated at Ti cathode. The electrolysis reaction is expressed as[4,5],



In total,



The reaction described above permits the recycling of the reducing agent Ca and the continuous reduction in the same molten CaCl_2 bath.

This OS process was successfully applied to the reduction of single oxides, such as TiO_2 and V_2O_5 [6], and the alloying of Ti-V-Cr and Ti-6Al-4V[7]. In this work, we tried to produce TNTZ alloy experimentally by using Eq. 1, and analyzed the residual oxygen concentration and the elemental distribution in the obtained samples.

Experimental

Fig. 1 shows the experimental apparatus for the electrolysis. The electrolyte was molten CaCl_2 which dissolved 0.5mol%CaO. The oxide powders (TiO_2 , Nb_2O_5 , Ta_2O_5 , and ZrO_2) were weighted at the targeted composition with the mass ratio of Ti-29Nb-13Ta-4.6Zr, and were mixed thoroughly in mortar, and then inserted into a cylindrical basket-like cathode made of Ti-net. The vessel shown in Fig. 1 was evacuated at 873K for about 30ks to remove water in the electrolyte.

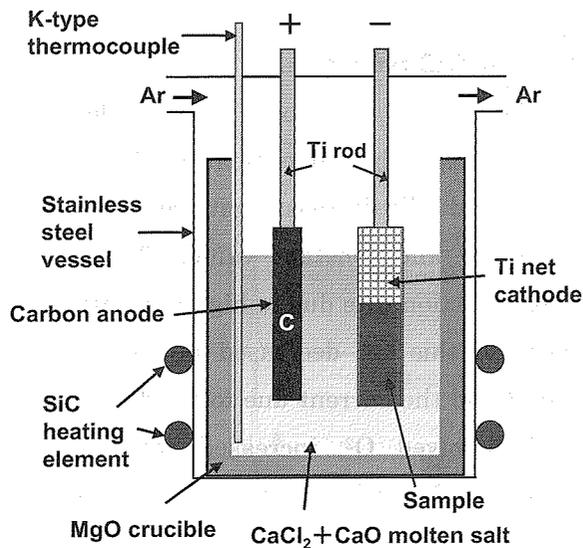


Fig. 1 Experimental apparatus.

Electrolysis was operated under the constant potential of 3.2V at 1173K in Ar gas atmosphere. The current was measured as a function of electrolysis time. Supplied charge, Q , was calculated by integrating current against time, and the theoretical charge, Q_0 , was defined as electricity to generate the stoichiometric amount of Ca for Eq. 1. The value of Q/Q_0 was controlled within 0~400%.

After the electrolysis, the cathode was pulled out from the bath and cooled in Ar. The sample in the Ti-net cathode was washed with distilled water, acetic acid, ethanol, acetone in this turn, and then analyzed by X-ray diffractometry (XRD), Electron probe microanalysis (EPMA), and oxygen analyzer.

The reduced powder samples were sintered for future application in powder metallurgy. It was pressed into pellet (ϕ 10mm and a few mm thick) at 450MPa and then sintered in Ar at 1300K for 54ks.

Results and discussion

Current density and XRD results

Fig. 2 shows the change of anodic current density during the electrolysis. The current showed comparatively large value at the initial stage, then gradually decreased with some bumps and finally it approached to a low and constant value. The large current was attributed to high reaction rate due to high concentration of dissolved O^{2-} . The amount of this O^{2-} decreased during the electrolysis as indicated in Eq. 2 and the current due to O^{2-} decreased. By contrast, the amount of dissolved O^{2-} increased when the reduction or deoxidation occurred effectively because the large amount of CaO was generated. These changes of the dissolved O^{2-} attributes to the current bumps. After complete reduction and removal O^{2-} , the current should be null. As shown in Fig. 2, however, a certain constant current was

found even at the final stage. This is due to the occurrence of parasite reactions that Ca reduces CO and CO₂ gas evolving at the anode.

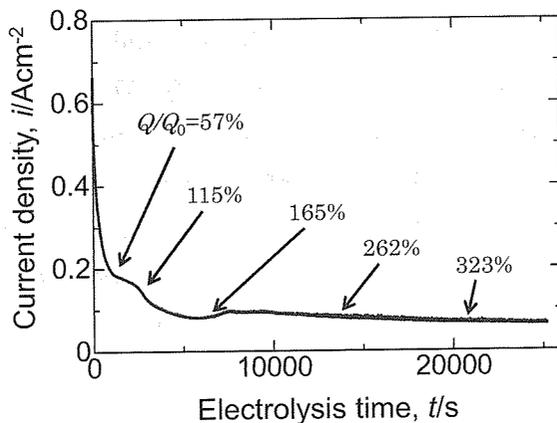


Fig. 2 Current density and electrolysis time.

Fig. 3 shows the XRD results of the reduced samples. In Fig. 3, α and β are HCP and BCC solid solutions, respectively.

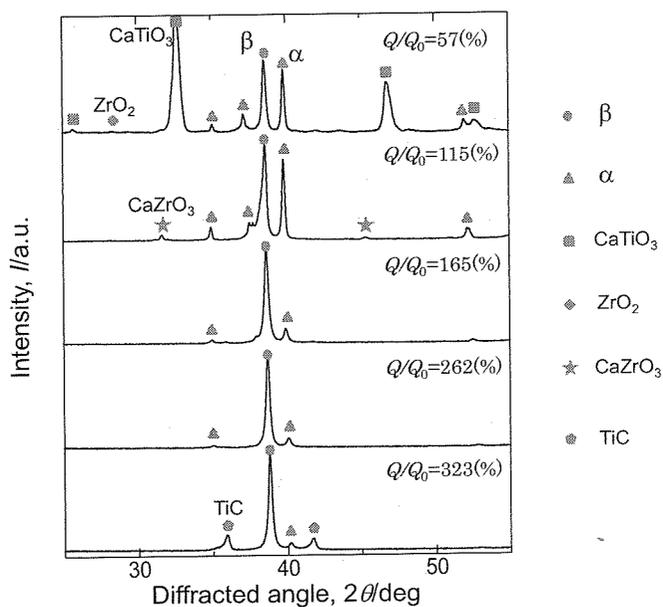


Fig. 3 XRD patterns of reduced samples.

It is clearly conducted from Figure 2 and 3 that the reaction during electrolysis was separated into the several stages. The reduction of Nb and Ta occurred at the initial stage of electrolysis ($Q/Q_0=0\sim 57\%$) and CaTiO_3 was also formed. Then its reduction and the generation of CaZrO_3 occurred at the second stage ($Q/Q_0=57\sim 115\%$). Both the reduction of CaZrO_3 and the transformation of α to β occurred at the third stage ($Q/Q_0=115\sim 165\%$), and only the latter reaction proceeded until the late stage ($Q/Q_0=165\sim 323\%$). It was also found that the formation of TiC occurred only at the final stage ($Q/Q_0=262\sim 323\%$). At all the stages, the residual α phase was detected while the reported TNTZ alloy had β single phase[8].

Oxygen concentration

Fig. 4 shows the relationship between the oxygen concentration of obtained sample and the supplied charge. The oxygen concentration decreased as the supplied charge increased, and finally it reached 1900mass ppm at $Q/Q_0=323\%$.

The reduction and deoxidation did not complete at $Q/Q_0=100\%$ and the deoxidation was suppressed at the later stage of electrolysis. These are caused by Ca consumption due to occurrence of parasite reactions (the reduction of CO or CO_2 gas) described before.

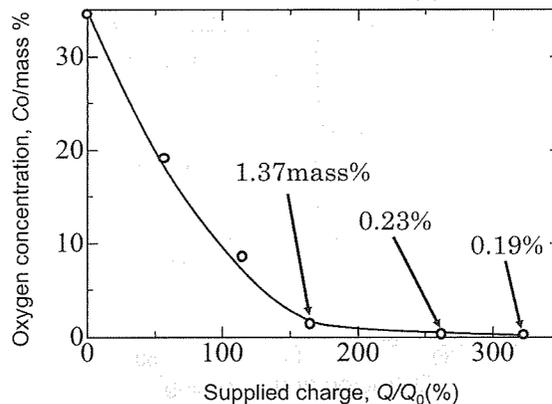


Fig. 4 Oxygen concentration and the supplied charge.

Element distribution

Table 1 and 2 show the results of local element analyses at the 8 positions in the sample which had 2300 mass ppm oxygen (obtained at $Q/Q_0=262\%$) and in the sintered pellet which was made from the same powder, respectively. Table 1 shows that the composition of reduced sample was slightly localized probably because of the coexistence of α phase. However, as shown in Table 2, the compositional homogeneity was improved and the analyzed compositions became close to the targeted value after sintering.

Table 1 Element analyses of powder.

	concentration, C/mass %			
	Ti	Nb	Ta	Zr
TNTZ	53.4	29	13	4.6
a	46.9	36.1	13.4	3.6
b	48.1	33.6	14.4	3.9
c	39.4	44.0	10.8	5.8
d	47.2	25.5	22.1	5.2
e	50.7	23.5	21.4	4.4
f	66.2	19.8	9.0	5.0
g	68.5	18.8	7.8	4.9
h	71.6	16.3	7.2	4.9
Average	54.8 ± 12.1	27.2 ± 9.8	13.3 ± 5.8	4.7 ± 0.7

Table 2 Element analyses of sintered pellet.

	concentration, C/mass %			
	Ti	Nb	Ta	Zr
TNTZ	53.4	29	13	4.6
a	54.2	27.4	14.1	4.3
b	53.0	28.5	14.4	4.1
c	53.8	27.7	14.0	4.5
d	54.2	27.3	14.2	4.3
e	59.4	29.7	6.3	4.6
f	62.2	20.5	13.7	3.6
g	52.9	27.7	14.8	4.6
h	53.4	28.1	14.1	4.4
Average	55.4 ± 3.4	27.1 ± 2.8	13.2 ± 2.8	4.3 ± 0.3

Fig.5 shows the XRD patterns of the powder (not sintered), of the sintered pellet, and of the reported pattern. It was recognized that the sintered sample had β single phase and that its XRD pattern conformed to that of the previous study [8].

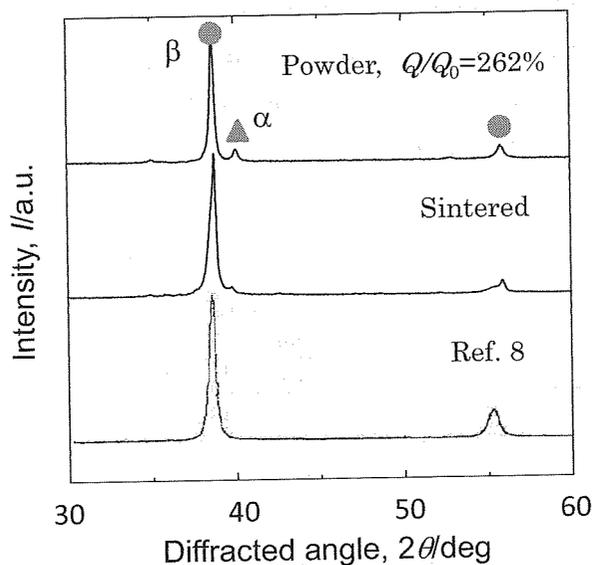


Fig. 5 XRD patterns.

Reaction procedure

Through these experiments, it was found that the reaction proceeded through the several stages during the electrolysis.

At about $Q/Q_0=0\sim 57\%$; The amount of O^{2-} in the melt decrease rapidly just after starting the electrolysis. Mainly Nb_2O_5 and Ta_2O_5 were reduced and the formation of $CaTiO_3$ proceeded.

At $Q/Q_0=57\sim 115\%$; The decomposition and reduction of $CaTiO_3$ and formation of $CaZrO_3$ occurred.

At $Q/Q_0=115\sim 165\%$; The reduction of $CaZrO_3$ and the transformation of α to β occurred. However, even at the end of this stage, α phase still

existed because both Ti and Zr localized due to the delayed reduction rate. The current dimple was often found in this stage. This may show that the first products α and β were covered by CaZrO_3 and that this coating inhibited the deoxidation and the alloying more extensively.

At $Q/Q_0=165\sim 262\%$; The decrease of oxygen concentration shows that the deoxidation of α and β phases occurred.

At $Q/Q_0=262\sim 323\%$; The current density was similar with that of the previous stage. However, the decrease of oxygen concentration suppressed. This means that the reduction of CO or CO_2 gas was dominant and that TiC precipitated.

In a short summary of the above discussion, 4 kinds of oxides were reduced to the metallic state and formed an alloy. They were not reduced independently, but not simultaneously in the microscopic scale.

Conclusions

The Ti-29Nb-13Ta-4.6Zr alloy was directly produced from the oxide mixture of TiO_2 , Nb_2O_5 , Ta_2O_5 , and ZrO_2 in the molten CaCl_2 by using OS process. The results are summarized as follows

1. The oxygen concentration decreased monotonically as the electrolysis time increased, and achieved to 2300 mass ppm without TiC precipitation.
2. The reduced sample with the low oxygen concentration was a mixture of α and β phases and was locally inhomogeneous due to the difference of reaction rate of componential oxides. However, after sintering, it became β single phase with the targeted compositions.

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