PREPARATION AND CHARACTERIZATION OF EXTRA-LOW-OXYGEN TITANIUM

T.H.Okabe, M.Nakamura, T.Ueki, T.Oishi and K.Ono

Department of Metallurgy, Kyoto University,
Yoshida Honmachi, Sakyo-ku, Kyoto 606, JAPAN

Abstract

Removal of oxygen in titanium by reaction with chemically active calcium dissolved in $CaCl_2$ was examined at temperatures between 1173 and 1473K with the purpose of obtaining extra-low-oxygen titanium. $CaCl_2$ was used as a flux to facilitate the reaction by decreasing the activity of the by-product CaO. Titanium wires and small pieces of titanium were deoxidized to 20 - 60 mass ppm oxygen by use of calcium-saturated $CaCl_2$.

Trace element analysis, micro Vickers hardness measurements, and electrical resistivity measurements were carried out to characterize the deoxidized titanium. Titanium with a high residual resistivity ratio ($\rho_{298}/\rho_{4.2}=100$) was produced by the deoxidation of electrolytically refined titanium. The "ideal resistivities", or hypothetical resistivities of pure titanium, at 77 and 298K were determined to be 40 and 440 nΩm, respectively. The influence of oxygen on resistivity at 4.2K was also measured by using titanium containing 30 and 500 mass ppmO, and was determined to be 88 nΩm/at%O.

As an alternate method for deoxidation, titanium wire was immersed into molten $CaCl_2$. Titanium and carbon electrodes acted as cathode and anode, respectively, using an external DC source. By this procedure, it is believed that the calcium potential in $CaCl_2$ increased at the titanium surface. Oxygen dissolved in the salt bath through deoxidation of titanium reacted at the carbon anode to form CO (or CO_2) gas and was removed from the system. The titanium samples in the salt were deoxidized by the electrolytically-produced calcium, and oxygen in titanium was lowered to below the 20 mass ppm level whereas the carbon concentration was increased to some extent.

Introduction

Over the past several years, the demand for high purity titanium for use in electronic materials has increased. For applications such as target materials for semiconductor use, 4 to 5N (excluding gaseous elements) high purity Kroll titanium has been mainly employed. More recently, for electronic materials use, titanium is purified further by using method of the iodide process(1) or electrolytic refining(2). The level of purity of titanium produced in these ways is between 5 and 6N (excluding gaseous elements), with the major impurity of 6N titanium being oxygen at about 100 mass ppm.

Among the known purification processes (e.g. electrolysis in molten salts, electron beam floating zone melting, electro-transport, and degassing in ultra high vacuum), no effective methods other than electrolytic refining and iodide refining have been developed for oxygen removal to a level below 100 mass ppm. Even if low oxygen titanium is successfully produced using these optimized methods, contamination by oxygen is inevitable during subsequent processing, such as during electron beam melting.

Oxygen removal directly from titanium-oxygen solid solution to a level below 50

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mass ppm is deemed to be very difficult because titanium has a strong affinity for oxygen. For this reason the conventional titanium refining process is based on reaction of oxygen free titanium compounds in a gas-tight system. From a thermodynamic view point, external gettering used for solid state refining is one of the most promising methods for direct deoxidation of titanium(3). This method can be applied during final deoxidation of titanium products as a surface deoxidation treatment following machining.

This paper reports the results of an experimental investigation directed towards the preparation of extra-low-oxygen titanium by using the calcium saturated $CaCl_2$ flux deoxidation method.(3)(4) As an alternative, an electrochemical deoxidation technique(5) was applied for producing oxygen-free-titanium. Characterization of the resulting degree of purity was made by trace element analyses, micro Vickers hardness measurements, and electrical resistivity measurements.

Calcium-Halide Flux Deoxidation Process

Principle

It is well known that a large amount of oxygen dissolves in titanium to form an interstitial solid solution. The maximum solubility of oxygen in hexagonal close-packed titanium (α-Ti) is about 33mol%.(6) The oxygen solubility in the high temperature bcc phase (β-phase) is much lower (about 2mol% at 1273K) and the α-β transformation temperature increases sharply with increasing oxygen content.

In this study, titanium deoxidation by reaction with a chemically active element, namely calcium dissolved in $CaCl_2$ through surface contact, was examined in the temperature range 1273 to 1473K, to obtain low oxygen-containing titanium. Calcium is thought to be the most effective deoxidation agent not only because it has an extremely strong affinity for oxygen but because it has a high vapor pressure around 1273K (P_{Ca}=1.9kPa)(7) and can diffuse into $CaCl_2$. Furthermore the maximum solubility of calcium in titanium is reported to be only about 60 mass ppm at 1273K.(8) $CaCl_2$ was used as a flux to contain the deoxidation agent calcium and in addition, to facilitate the reaction by diluting the reaction product CaO, i.e., decreasing the activity of the by-product CaO.

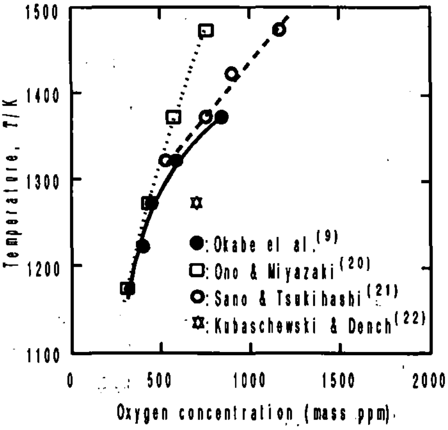

Figure 1 – Equilibrium oxygen concentration in Ti under Ca–CaO existence.(9)

Since details of the principle of calcium-halide flux deoxidation of titanium are reported elsewhere(3), only a brief outline will be given here. Titanium-oxygen solid solution can be deoxidized by calcium to a lower oxygen level by the following reaction:

$$\text{O (in Ti)} + \text{Ca (in flux)} = \text{CaO (in flux)} \qquad (1)$$

Co-existence of calcium and the by-product, CaO, fixes the equilibrium oxygen partial pressure, and hence, the amount of residual oxygen in titanium is thermodynamically determined. The deoxidation limit of titanium is given by Equation (2) at temperature T.

$$[\%O] = (a_{CaO}/a_{Ca})(1/f_O)\exp(\Delta G^o/RT) \qquad (2)$$

where ΔG^o is the standard free energy change of Equation (1), a_{CaO} and a_{Ca} are the activities of CaO and calcium, respectively, and f_O is the activity coefficient of oxygen in solid titanium. When determining the partial pressure of oxygen in β-solid titanium, the authors measured the equilibrium oxygen concentration in titanium coexisting with calcium and CaO at temperatures between 1173K and 1373K(9). Based on these obtained data, and the condition that the activity of the by-product CaO is unity, the predicted deoxidation limit of titanium by using pure calcium at 1273K is about 500 mass ppm as shown in Fig.1(9). The authors also discussed the feasibility of preparation of low oxygen-containing titanium by decreasing the activity of the by-product CaO using various calcium-halide fluxes in the presence of calcium metal. After consideration of several factors in choosing a flux and the process parameters for deoxidation, $CaCl_2$ was decided to be the most suitable among many halide fluxes around 1300K⁽³⁾. $CaCl_2$ used as a flux dissolves a large amount of CaO (about 20 mol% at 1273K ⁽¹⁰⁾), while the solubility of $CaCl_2$ in calcium is less than 5 mol%⁽¹¹⁾. Therefore, it is expected that the CaO by-product of deoxidation will be dissolved by the calcium-saturated $CaCl_2$ flux, and that the deoxidation limit will be lowered as the activity of CaO (refer to Equation (2)) is decreased. For example, Equation (2) shows that when the activity of CaO in the flux is decreased to a level of 0.01 in the presence of calcium, the deoxidation limit is lowered to the 5 mass ppm level at 1273K.

Experimental

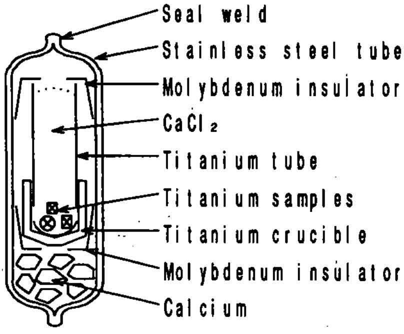

Figure 2 - Schematic illustration of the reaction tube.

Fig.2 shows the arrangement of the reaction tube used for titanium deoxidation in this study. Ten to fifteen titanium samples (about 0.1 - 2g each) were placed on a titanium dish within a titanium cup, which was filled with about 20g of $CaCl_2$. The $CaCl_2$ used in this study was reagent grade anhydrous $CaCl_2$ (99.9%) in powder form, dried at 800K for more than 200ks. Several kinds of titanium pieces and wires with different oxygen concentration and configuration were used as starting materials. The cup containing the titanium sample and $CaCl_2$ was sealed in a stainless steel tube with 5g of calcium granules, as shown in Fig.2. To avoid contamination of the sample by impurities in calcium (mainly CaO and nitrogen), calcium was isolated from the samples and flux, and supplied to the flux in vapor form.

The assembled sealed tube was heated in an electric furnace to a temperature between 1173 and 1473K. The holding time was between 86.4ks and 260ks, after which, the reaction tube was taken out from the furnace and quenched in water. The amount of time necessary to reach equilibrium was determined in previous work⁽⁹⁾. In some experiments, for the purpose of annealing, the reaction container was cooled in the furnace, or quenched and then heated again to 1073K for 10ks to remove defects in the samples which would interfere in resistivity measurements. After heat treatment, the calcium-saturated fused salt in the titanium cup was removed by leaching with (1+1) acetic acid, and the resulting titanium samples were carefully cleaned in warm HCl aqueous solution followed by water, alcohol and acetone, and then allowed to dry.

Oxygen and nitrogen analyses of the samples were made using an inert gas fusion infrared absorption method (LECO TC-336 analyzer). For oxygen and nitrogen extraction, 0.1g of titanium sample enclosed in 1g of platinum foil was dropped into a graphite crucible and held at a temperature above 2800K. Electrical resistivity measurements were carried out on samples in wire-form which were immersed in liquid helium, liquid nitrogen, and water kept at 298K. The conventional four probe direct current technique was adopted. Micro Vickers hardness measurements using a 500 g load were carried out at room temperature on the chemically polished surfaces of cross sectioned samples. Trace element analysis of titanium was carried out utilizing glow discharge mass spectroscopy(GDMS), and in the case of calcium, the values were cross checked by using flameless atomic absorption spectroscopy.

Results and Discussion

Oxygen and nitrogen analysis Some representative analytical oxygen and nitrogen concentrations in titanium before and after experiments are listed in Table I.

By using Ca-$CaCl_2$ flux, titanium samples were deoxidized to a level below 50 mass ppm, and in some experiments the oxygen contents in titanium were lowered to less than 20 mass ppm. The final oxygen concentrations were essentially independent of the initial oxygen concentrations under these experimental conditions. The reaction periods appear to be sufficient to reach equilibrium, and thus, the deoxidation limit in these experiments may be determined from the activity of CaO in the flux. It is believed that, in this study, the amount of

CaO derived from deoxidation of titanium was small in comparison to the level of CaO impurity in $CaCl_2$. For further deoxidation, it seems necessary to refine the $CaCl_2$ for CaO elimination.

Table I Results of titanium deoxidation by the calcium-halide flux deoxidation method.

Exp. condition Temperature / Holding time	Oxygen conc. (mass ppm) Initial	Oxygen conc. (mass ppm) After exp.	Nitrogen conc. (mass ppm) Initial	Nitrogen conc. (mass ppm) After exp.	Vickers hardness (kgf/mm^2) After exp.	RRR ($\rho 298/\rho 4.2$) After exp.
1273K / 86ks	900+	80	100	130	103	17
1273K / 90ks	130*	16	10	41	85	100
	130*	17	10	34	-	100
	200	23	20	52	79	-
1373K / 86ks	110*	37	5	48	86	120
1373K / 40ks	130*	35	10	49	93	95
	130*	22	10	45	-	-

* : Electrolytically refined titanium, + : Commercial grade titanium.

Nitrogen concentrations in the samples were independent of the experimental conditions, and increased from the initial values by about 40 mass ppm, in all cases. This increment seems to be caused by residual nitrogen in the reaction tube and/or the presence of nitrogen in the $CaCl_2$ and calcium, since no nitrogen gas elimination was done preceding the sealing of the sample in the reaction tube.

Micro Vickers hardness measurements The micro Vickers hardness value of electrolytically refined titanium was 80–90 kgf/mm^2 following deoxidation. Typical hardness values are also listed in Table I.

Trace elements analysis Results of GDMS indicate that calcium, chromium and nickel concentrations remained unchanged with the deoxidation treatment. The calcium concentration of the deoxidized samples were cross checked by using an atomic absorption method: the analyzed values ranged from 0.8 to 1.2 mass ppm. Detailed analysis of trace metal impurities in titanium before and after deoxidation are provided in a previous work.(4)

Residual resistivity ratio measurements The resistivity ratios, $\rho_{298}/\rho_{4.2}$(=RRR) and ρ_{298}/ρ_{77}, are fairly accurate, since values do not include error associated with size measurements. The RRR values increased in all cases following deoxidation treatment. It is worth noting that the RRR value for electrolytically refined titanium wire reached a magnitude of hundred after deoxidation, while that for commercial grade titanium wire showed only about 17 as shown in Table I.

In general, the resistivity of titanium at temperature T, ρ_T, can be put in the form

$$\rho_T = \rho_{i,T} + \rho_0 + \Delta_{T,C} \qquad (3)$$

where $\rho_{i,T}$ is the "ideal resistivity" due to scattering of electrons by thermal vibration, ρ_0 is the residual resistivity at absolute zero (0 K) determined by impurities and lattice defects, and $\Delta_{T,C}$ is the deviation from Matthiessen's rule (DMR). The residual resistivity, ρ_0, is essentially equal to the resistivity at 4.2K, $\rho_{4.2}$, in the case of titanium because $\rho_{i,T} + \Delta_{T,C}$ is negligible compared to ρ_0.

Assuming that Matthiessen's rule can be applied, that is, $\Delta_{T,C}$ in Equation (3) is zero, values measurable with high accuracy can be expressed as follows;

$$\rho_{77} / \rho_{298} = (\rho_{i,77} + \rho_0) / (\rho_{i,298} + \rho_0) \qquad (4)$$

$$\rho_{4.2} / \rho_{298} = (\rho_{i,4.2} + \rho_0) / (\rho_{i,298} + \rho_0). \qquad (5)$$

The relationship between ρ_{77}/ρ_{298} and $\rho_{4.2}/\rho_{298}$ can be obtained by eliminating ρ_0 from Equations (4) and (5) as follows,

$$\rho_{77}/\rho_{298} = A\, \rho_{4.2}/\rho_{298} + B \qquad (6)$$

where A and B are $(\rho_{i,298}-\rho_{i,77})/(\rho_{i,298}-\rho_{i,4.2})$ and $(\rho_{i,77}-\rho_{i,4.2})/(\rho_{i,298}-\rho_{i,4.2})$, respectively. The values A and B in Equation (6) are constant, and independent of impurity concentration. Consequently, if Matthiessen's rule can be applied to titanium which contains dilute impurities, every pair of measured values (ρ_{77}/ρ_{298} and $\rho_{4.2}/\rho_{298}$) for the samples should fall on a straight line expressed by Equation (6), even though ρ_0 of these samples may be very large. Also the values, ρ_{77}/ρ_{298} and $\rho_{4.2}/\rho_{298}$, should approach the values, B and 0, respectively, as the purity of titanium increases (viz. ρ_0 approaches 0).

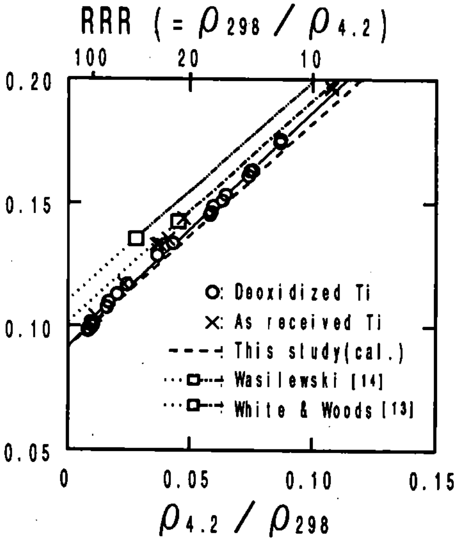

Figure 3 – Relationship between ρ_{77}/ρ_{298} and $\rho_{4.2}/\rho_{298}$ for deoxidized titanium wires.(4)

In Fig.3, measured values of ρ_{77}/ρ_{298} are plotted against $\rho_{4.2}/\rho_{298}$ for deoxidized titanium wires as well as for as-received titanium wires. The measured values for deoxidized samples fall on a straight line, but those for as-received titanium wires, especially for samples with high ρ_0 (high oxygen concentration), deviate from the straight line. This result indicates that the effect of oxygen on the term $\Delta_{T,C}$ in Equation (3) cannot be neglected, and that Matthiessen's rule cannot be applied to titanium with high oxygen concentration. From the 24 pairs of measured values for deoxidized titanium wires, the constants (Equation (7)), A and B were calculated using the least square approximation, and are depicted by the solid line in Fig 3.

$$\rho_{77}/\rho_{298} = 0.951\,\rho_{4.2}/\rho_{298} + 0.0918 \quad (7)$$

The sum of A and B in Equation (6) should theoretically be one, whereas the measured value in Equation (7) is 1.04. This 4 percent discrepancy is somewhat large and cannot be attributed solely to experimental error, and seems to be due to DMR of samples with some impurities in addition to oxygen. That is to say, not only oxygen but also other impurities contribute to DMR for titanium to some extent. For a more rigid discussion concerning DMR, titanium purified further to a lower ρ_0 value is needed, and effect of hydrogen on resistivity must also be considered (12).

Ideal resistivities of titanium In Table II, the ideal resistivities at 77 and 298K were calculated by using deoxidized samples on the assumption that $\Delta_{T,C}$ in Equation (3) is negligible for samples with RRR of about one hundred. The data obtained by White and Woods (13) and by Wasilewski (14) are also listed for comparison. By using the values in Table II, the constants A and B in Equation (6) can be calculated. Calculated relationships between ρ_{77}/ρ_{298} and $\rho_{4.2}/\rho_{298}$ are illustrated in Fig.3 along with their respective literature value (□). The dashed line in Fig.3 is calculated using the values in Table II obtained in this study. There is a large discrepancy between the three calculated lines, probably due to DMR. That is, in the calculation of $\rho_{i,T}$ in Equation (3) using a sample with large ρ_0, it is unavoidable that there is contribution of $\Delta_{T,C}$ to $\rho_{i,T}$. Therefore, it seems necessary to use as low residual resistivity as possible to minimize the interference by DMR in the determination of the ideal resistivity.

Table II Ideal resistivity of titanium at 298 and 77K.

	$\rho_{i,298}$ (nΩm)	$\rho_{i,77}$ (nΩm)	ρ_0 (nΩm)	Note	Ref.
White & Woods	437*	44.5+	19.7	$\rho_{i,273}$ = 390 nΩm	13
Wasilewski	461+	50.9	13.1	$\rho_{i,273}$ = 414 nΩm	14
G.Elssner et al.	430			210 ppmO, 20 ppmN	17
This study	440	40	4.6	30 ppmO, 50 ppmN	4

* : Extrapolated, + : Interpolated

Influence of oxygen on electrical resistivity The contribution by oxygen to the resistivity of titanium, $\Delta\rho/c$, determined in this study, as well as from the literatures, is given in Table III.(15-19) The calculated value, 88 nΩm/mol%O, using the data for electrolytically refined high purity titanium, which contained 28,17,22 and 500 mass ppm oxygen is in fairly good agreement with the reported data.

Table III Contribution of oxygen to the resistivity of titanium at several temperatures for various oxygen concentration ranges. ρ_T is the resistivity with lowest oxygen concentration at the measured temperature.

	$\Delta\rho/c$ (nΩm/mol%O)	T (K)	ρ_T (nΩm)	Oxygen conc. range (mol%O)	Ref.
Ames & McQuillian	113	293	470	- 1.5	15
Wasilewski	123	273	427	0.13 - 10	16
Elssner et al.	82	298	430	0.063 - 1.0	17
Komatsu et al.	101	77	60.6	0.890 - 3.2	18
Baur & Lehr	103	20.4	2.68	0.009 - 0.32	19
This study	88	4.2	4.60	0.009 - 0.15	4

An Electrochemical Deoxidation Technique

Principle

In the calcium-halide flux deoxidation process mentioned above, there exist strict limitations on the purity of flux and the initial oxygen content of the titanium used, since the ultimate limit of deoxidation is dependent on the amount of oxygen present as an impurity in the flux and on the amount of CaO produced during deoxidation.

An alternate method for deoxidation, expressed schematically in Fig.4, is characterized by both production of calcium deoxidant from the flux and by effective removal of O^{2-} (mainly present as CaO in the flux) dissolved in the flux by means of an electrochemical technique.(5) The deoxidation reaction given in Eq.(1') is thus facilitated. By the method developed in this study, titanium in the vicinity of the titanium cathode is deoxidized by calcium which is produced electrochemically on the surface of the cathode according to Eq.(8). According to the cathodic reaction, O^{2-} species in the flux, present as impurities or as the deoxidation product CaO, are continuously transported for reaction at the carbon anode, and oxygen in the flux is removed from the system as CO (or CO_2) gas by the anodic reaction expressed in Eq.(9).

$$\text{O (in Ti)} + \text{Ca (in flux)} = \text{Ca}^{2+}\text{ (in flux)} + \text{O}^{2-}\text{ (in flux)} \qquad (1')$$

$$\text{Ca}^{2+}\text{ (in flux)} + 2e^- = \text{Ca (on Ti cathode : in flux)} \qquad (8)$$

$$\text{O}^{2-}\text{ (in flux)} + \text{C (carbon anode)} = \text{CO (gas)} + 2e^- \qquad (9)$$

Unlike the calcium-halide flux deoxidation process, metallic calcium is not necessary as a deoxidant since the activity of calcium near the cathode can be increased by controlling the applied voltage between the titanium cathode and carbon anode, such that deoxidation is effected. In some cases, calcium can even be precipitated on the cathode. That is, this electrochemical method has another advantage in that elimination of impurities originating

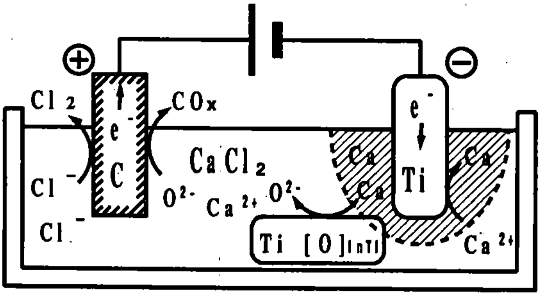

Figure 4 – Deoxidation of titanium using an electrochemical technique.

from metallic calcium deoxidant is not a concern.

Experimental

A schematic illustration of the apparatus used in the electrochemical deoxidation method is shown in Fig.5. $CaCl_2$ flux which had been previously dehydrated at 473K under vacuum was heated to 1173K. A titanium cathode and glassy carbon anode were then inserted into the molten $CaCl_2$ flux. Deoxidation of titanium cathodes consisting of titanium samples of various oxygen concentrations (200−1400 mass ppmO) was effected using an applied voltage between 2 and 6V for a time greater than 18ks. The titanium samples obtained were subjected to oxygen, nitrogen and carbon analyses using LECO analyzers. For the purpose of increasing the accuracy of the oxygen and nitrogen analyses, 1g of platinum foil containing 4.5±1.0μg oxygen was used as an extraction bath for each 0.1g titanium sample.

Results and Discussion

Some representative results of the experiments are listed in Table IV. Deoxidation of titanium was performed effectively. Titanium samples were successively deoxidized to a level below 50 mass ppmO during a reaction period of several hours. Among the deoxidized samples, some oxygen-free-titanium samples were obtained, that is, titanium containing oxygen below the detection limit(about 10 mass ppmO) of analysis was produced.

The carbon concentration was considerably increased after reaction(Exp.no.49) By implementing a titanium partition wall with bored holes between the cathode and anode(Exp.no.17), or by regulating the applied voltage between electrodes(Exp.no.46,44,21), the increase in carbon was lowered.

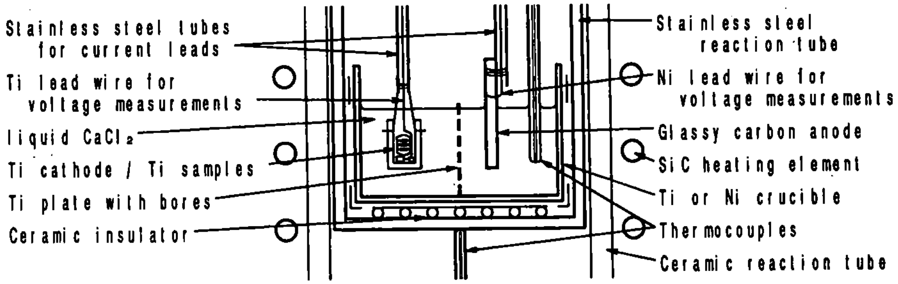

Figure 5 − Schematic illustration of the apparatus used in the electrochemical deoxidation method.

Table IV Results of titanium deoxidation using an electrochemical technique.

Exp. no.	Experimental conditions	Oxygen conc. (mass ppm)		Nitrogen conc. (mass ppm)		Carbon conc. (mass ppm)	
		Initial	Afer exp.	Initial	Afer exp.	Initial	Afer exp.
49	1223K / 22ks 3.5V / 1.8A	900 1400	<10 <10	40 20	40 20	30 50	900 670
17*	1173K / 23ks 4.0V / 1.8A	900	60	20	20	30	60
46	1223K / 22ks 3.0V / 0.27A	140 1400	100 60	<10 20	<10 20	20 50	20 50
44	1223K / 22ks 2.8V / 0.50A	900	50	40	40	50	60
21	1173K / 27ks 2.8V / 0.40A	900 1400	<10 100	20 20	20 50	30 50	30 70

* : Ti plate with bored holes was implemented between electrodes.

Conclusions

Titanium in the form of wires and small pieces was deoxidized to a level of 20 - 60 mass ppm oxygen by use of calcium-saturated $CaCl_2$ flux at 1273K. The micro Vickers hardness value of electrolytically refined titanium was 80-90 kgf/mm^2 following deoxidation. The calcium concentration in titanium remained unchanged.

Resistivity measurements were carried out at 4.2, 77 and 298K on titanium wires. Deviation from Matthiessen's rule was observed for titanium samples with high residual resistivity. By deoxidizing electrolytically refined titanium wire, titanium with a high residual resistivity ratio ($\rho_{298}/\rho_{4.2}=100$) was produced, and the ideal resistivities at 77 and 298K were determined to be 40 and 440 nΩm, respectively. The contribution by oxygen to resistivity at 4.2K was also measured by using titanium samples obtained in this study, and determined to be 88 nΩm/mol%O.

An alternate method for removing oxygen dissolved in titanium was also developed. Titanium containing several hundred mass ppm oxygen could be deoxidized to a level below the detection limit of oxygen analysis (about 10ppm) by using the electrochemical technique.

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