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Preparation and characterization of extra-low-oxygen titanium

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Abstract

Removal of oxygen in titanium by reaction with chemically active calcium dissolved in $CaCl_2$ was examined between 1273 and 1473 K 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 $CaCl_2$ at a temperature of 1273 K.

Trace element analysis (*e.g.* glow discharge mass spectrometry), micro Vickers hardness measurements, and electrical resistivity measurements were carried out to characterize the deoxidized titanium. The deoxidation of electrolytically refined titanium wire produced titanium with a high residual resistivity ratio ($\rho_{298}/\rho_{4.2} \simeq 100$). The "ideal resistivities", or hypothetical resistivities of pure titanium, at 77 and 298 K were determined to be 40 and 440 nΩm respectively. The influence of oxygen on resistivity at 4.2 K was also measured by using titanium containing 30 and 500 mass ppm O, and was determined to be 88 nΩm (mol.% O)$^{-1}$.

1. 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 uses, 99.99–99.999% (excluding gaseous elements) high purity Kroll titanium has been mainly employed. More recently, for electronic-material use titanium is purified further by using the iodide process method [1] or electrolytic refining [2]. The level of purity of titanium produced in these ways is between 99.999 and 99.9999% (excluding gaseous elements), with the major impurity of 99.9999% 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 50 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 (EB) melting.

Oxygen removal directly from titanium–oxygen solid solution to a level below 50 mass ppm is deemed to be very difficult because titanium has a strong affinity for oxygen. For this reason the titanium refining process is based on the reaction of oxygen-free titanium compounds in a gas-tight system. From a thermodynamic viewpoint, 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 to the final deoxidation of titanium products as a surface deoxidation treatment following machining.

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 1273–1473 K, 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 1273 K ($P_{Ca} = 1.9$ kPa) [4] and can diffuse into $CaCl_2$. Furthermore the maximum solubility of calcium in titanium is reported to be only about 60 mass ppm at 1273 K [5]. $CaCl_2$ 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.

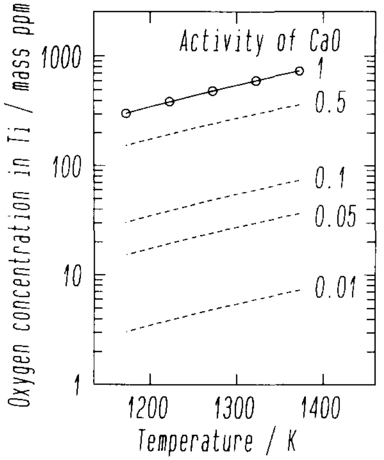
Since the principle of calcium–halide flux deoxidation for titanium is reported in detail elsewhere [3], only a brief outline will be given here. Titanium–oxygen solid solution can be deoxidized by calcium to a lower oxygen level by the following reaction:

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

Coexistence of calcium and the by-product, CaO, fixes the equilibrium oxygen partial pressure, and hence the amount of residual oxygen in titanium is thermodynamically decided. The deoxidation limit of titanium is given in eqn. (2) at constant temperature T:

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

where ΔG° is the standard free energy change of eqn. (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 1173 and 1373 K [6]. 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 1273 K was 500 mass ppm, as shown in Fig. 1 [6]. 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. Several factors have been considered in choosing a flux and the process parameters for deoxidation, and $CaCl_2$ appears to be the best flux among many halide fluxes around 1300 K [5]. $CaCl_2$ used as a flux dissolves a large amount of CaO (about 20 mol.% at 1273 K [7]), while the solubility of $CaCl_2$ in calcium



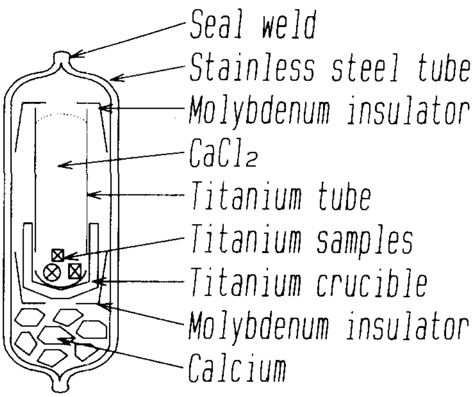


Fig. 1. Equilibrium oxygen concentration in β-Ti under the existence of Ca. The curves indicate the deoxidation limits of titanium as a function of temperature and activity of CaO using calcium-saturated flux.

Fig. 2. Schematic illustration of the reaction tube.

is less than 5 mol.% [8]. It is, therefore, 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 eqn. (2)) is decreased. For example, Fig. 1 illustrates 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 1273 K.

This paper reports the results of an experimental investigation directed towards the preparation of extra-low-oxygen titanium by using the Ca–$CaCl_2$ flux deoxidation method. Characterization of the resulting purity was made by micro Vickers hardness measurements, trace element analysis, and electrical resistivity measurements.

2. Experimental details

Figure 2 shows the arrangement of the reaction tube used for titanium deoxidation in this study. Ten to fifteen titanium samples (about 0.1–2 g each) were placed on a titanium dish within a titanium cup, which was filled with about 20 g of $CaCl_2$. The $CaCl_2$ used in this study was reagent grade anhydrous $CaCl_2$ (99.9%) in powder form, dried at 800 K for more than 200 ks. As shown in Table 1 several kinds of titanium pieces and wires with different oxygen concentrations and configurations were used as starting materials. The cup containing the titanium sample and $CaCl_2$ was sealed in a stainless steel tube with 5 g of calcium granules, as shown in Fig. 2. To avoid contamination of the sample by impurities in calcium (mainly CaO),

TABLE 1

Some analytical values of titanium samples (electrolytically refined sponge, electron-beam (EB) melted) used for deoxidation experiments

Sample no.	Grade[a]	Oxygen conc. (mass ppm)	Nitrogen conc. (mass ppm)	RRR[b] ($\rho_{298}/\rho_{4.2}$)	H_V[b]	Configuration
A	99.9999%	110	5	88	131	2.9 mm ϕ wire
B1	99.9999%	130	10	27	224	1.8 mm ϕ wire
B2	99.9999%	130	10	24	–	0.9 mm ϕ wire
C	99.9999%	150	10	43	185	3.0 mm ϕ wire
D	99.9999%	260	20	28	116	3.9 mm ϕ wire
E	99.99%[c]	200	20	–	93	Small pieces
F	99.9%[d]	900	100	9.3	201	1.2 mm ϕ wire

[a] Excluding gaseous elements.
[b] Measured as received.
[c] EB melted high purity sponge.
[d] Commercial grade titanium.

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 1473 K. The holding time was between 86.4 ks and 260 ks, after which the reaction tube was taken out from the furnace and quenched in water. The amount of time necessary to reach equilibrium has been determined in previous work [6]. In some experiments, for the purpose of annealing the reaction container was cooled in the furnace, or quenched and then heated again to 1073 K for 10 ks 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 glossy 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). Preceding the oxygen and nitrogen analyses, the samples were chemically polished with a 1:4:10 mixture of $HF–HNO_3–H_2O$. For oxygen and nitrogen extraction, 0.1 g of titanium sample enclosed in 1 g of platinum foil was dropped into a graphite crucible and held at a temperature above 2800 K. The average blank values (mainly due to the platinum bath) of oxygen and nitrogen were 1.8 ± 0.2 μg and 0.2 ± 0.1 μg respectively.

Electrical resistivity measurements were carried out on samples in wire form which were immersed in liquid helium, liquid nitrogen, and water maintained at 298 K. The conventional four-probe d.c. technique was adopted using spot-welded Cu wires, 0.1 mm in diameter, as potential terminals. Sample currents were in the range 1–100 mA, and the potential difference at the terminals of the sample, proportional to the sample resistance, was measured by a voltmeter (Keithley Model K-181 nanovolt detector). In order to eliminate the contribution by thermal electromotive forces, the current polarity was reversed three times, and the mean of four readings was taken as the electromotive force value.

Micro Vickers hardness measurements using a load of 500 g were carried out at room temperature on the chemically polished surfaces of cross-sectioned samples. The samples were mounted in resin for polishing to make the planar surfaces, and the scratches inherited from mechanical polishing were chemically removed with HNO_3–HF solution. Grain boundaries were well etched by this acid.

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.

3. Results and discussion

3.1. Oxygen and nitrogen analysis

The analytical results for the oxygen and nitrogen concentrations in titanium before and after experiments are listed in Table 2.

By using Ca–$CaCl_2$ flux, titanium samples were deoxidized to a level below 100 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 in 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 in this study 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.

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 carried out preceding the sealing of the sample in the reaction tube. As calcium has a weaker affinity for nitrogen than titanium it is not possible to remove nitrogen from titanium by this method.

In order to produce titanium wires with no defects such as dislocations, samples in experiments 16, 17, 19 and 24 were annealed or cooled in the furnace following deoxidation, and then subjected to resistivity measurements. The samples of experiment 24 in Table 2 were heat treated using Ca–CaO at 1273 K for the purpose of producing titanium wire containing 500 mass ppm oxygen with the same nitrogen concentration as the others.

TABLE 2

Results of oxygen and nitrogen analyses of titanium samples deoxidized using Ca–CaCl$_2$

Experimental no.	Experimental condition: temperature (K)/holding time (ks)	Oxygen concentration (mass ppm)		Nitrogen concentration (mass ppm)		H_V (kgf mm^{-2}) after exp.
		Initial	After exp.	Initial	After exp.	
3-C	1273/86	150	62	10	86	81.9
3-D		260	61	20	63	81.9
3-E		200	63	20	93	87.2
3-F		900	80	100	130	103.0
4-A	1323/79	110	86	5	63	90.1
4-E		200	100	20	75	93.5
5-A	1373/86	110	37	5	48	85.7
5-E		200	43	20	59	81.7
6-A	1423/40	110	94	5	53	90.2
6-E		200	72	20	82	87.6
7-A	1473/43	110	63	5	41	87.7
7-E		200	63	20	50	83.4
16-B1	1273/90	130	27	10	51	89.2
16-B1		130	28	10	43	–
16-B2		130	34	10	65	–
16-E	(Annealed at 1073 K for 22 ks)	200	23	20	52	79.3
17-B1	1273/90	130	16	10	41	85.0
17-B1		130	17	10	34	–
17-E	(Annealed at 1073 K for 22 ks)	200	68	20	62	90.2
19-B1	1373/40	130	35	10	49	92.5
19-B1		130	22	10	45	–
19-B2	(Annealed at 1073 K for 65 ks)	130	27	10	92	–
19-E		–	–	–	–	89.9
24-B1	1273/86	130	500	10	53	125.0
24-B1		130	479	10	55	–
24-B2	Under Ca–CaO equilibrium	130	482	10	83	–
24-E	(Cooled in furnace)	200	474	20	77	114.0

3.2. Micro Vickers hardness measurements

Results of the micro Vickers hardness measurements are listed in the final column of Table 2. These values are plotted against oxygen concentration in Fig. 3. For samples produced from the same starting material, their hardnesses increases with increasing oxygen concentration.

The dashed lines in Fig. 3 are calculated from the data obtained by Okazaki and Conrad [9] on the assumption that the contribution of oxygen and nitrogen to the hardness of titanium solid solution are additive. The effect of grain size on hardness may be neglected because grain sizes of the deoxidized samples obtained in this study were more than 1 mm.

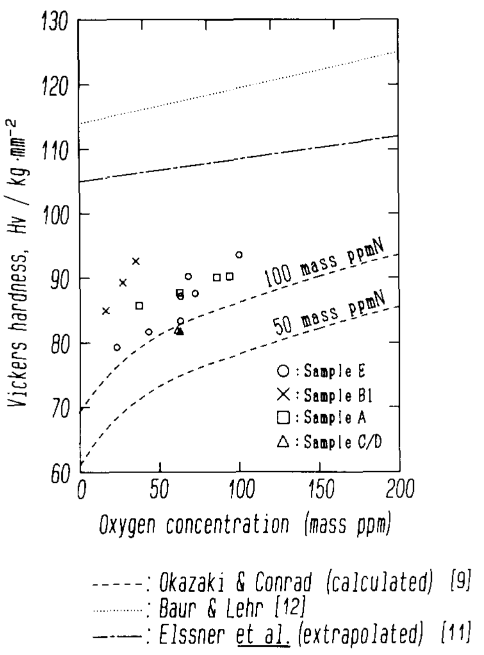


Fig. 3. Effect of oxygen on the hardness of titanium. Micro Vickers hardness measurements (load of 500 g) were performed on deoxidized titanium samples containing about 50 mass ppm nitrogen.

Considering the fact that the smallest hardness value measured by Okazaki and Conrad was 85 kg mm^{-2} for titanium containing 135 mass ppm O and 100 mass ppm N, the values for the deoxidized samples containing about 50 mass ppm nitrogen in this study are somewhat larger than the calculated values based on above mentioned assumption. When the oxygen contribution to hardness was derived, it was based on the oxygen analysis only, and nitrogen and carbon pick up during arc melting and heat were neglected [10]. It seems that the absolute values of hardness for titanium oxygen alloys, determined by them, include some uncertainty due to impurities other than oxygen, especially for very dilute oxygen alloys.

Data lines extrapolated from Elssner *et al.* [11] and Baur and Lehr [12] are also plotted in Fig. 3 for reference; however, these authors did not provide detailed information on grain size and nitrogen concentration. The scattering of the present data points in Fig. 3 may be due to the contribution of impurities other than oxygen. No clear interrelation between minute metallic impurities and hardness was found.

3.3. *Trace element analyses*

Analytical values of trace impurity element levels in titanium before and after deoxidation are listed in Table 3. From the results of GDMS it is notable that copper and silicon concentrations markedly increased after deoxidation. This is probably due to impurities in $CaCl_2$ which diffused into the titanium

TABLE 3

Impurity concentrations of titanium samples: metallic and carbon impurities were determined by glow discharge mass spectroscopy; oxygen and nitrogen by the method of inert gas fusion

Sample no.	Conditions	Concentrations of impurities in titanium (mass ppm)									Additional information	
		O	N	C[a]	Cu	Si	Cr	Fe	Ni	Ca	RRR	H_V
A	(as received)	107	5	2.5	0.98	1.6	0.15	0.16	0.04	1.0	88.8	131
4-A	1323 K, 79 ks	86	63	5.1	3.0	86	0.52	1.67	0.68	0.85	101	90.1
5-A	1373 K, 86 ks	37	48	2.9	2.56	45	1.1	1.50	0.14	1.2	119	85.7
6-A	1423 K, 40 ks	94	53	7.1	4.65	44	0.76	8.30	2.73	1.3	111	90.2
D	(as received)	260	20	1.4	0.38	0.69	0.19	0.19	0.04	1.5	21.1	116
3-D	1273 K, 86 ks	61	63	10	1.9	24	0.28	0.59	0.07	1.1	122	81.9
C	(as received)	150	10	1.9	0.75	1.0	0.18	0.16	0.05	1.2	43.1	185
3-C	1273 K, 86 ks	62	86	7.3	2.4	29	0.58	0.82	0.27	1.4	106	81.9
E	(as received)	200	20	5.0	0.90	3.1	13	8.94	15	1.4	–	105
5-E	1373 K, 86 ks	43	59	5.9	3.4	48	15	10	14	1.1	–	81.7

[a] Includes large uncertainty; listed for reference purposes only.

sample. As for chromium, nickel and calcium, the concentrations remained unchanged with the deoxidation treatment. The calcium concentration of the sample no. 5-E was cross-checked by using the atomic absorption method; the analyzed values ranged from 0.8 to 1.2 mass ppm. The carbon concentrations in Table 3 are listed only for reference since the associated uncertainties are rather larger because of the method of analysis.

Obinata *et al.* [5] reacted titanium powder with calcium in the temperature range 1118–1573 K, and obtained the solubility of calcium in titanium. The calcium solubility they reported, which is about 60 mass ppm, is large compared with the data in Table 3. As not much is known about the diffusivity of calcium in titanium, it is difficult to discuss these differences at this stage.

3.4. *Residual resistivity ratio measurement*

In Table 4 typical measured values of electrical resistivity of titanium wires are listed as well as the results of oxygen concentration and Vickers

TABLE 4

Results of resistivity measurements of deoxidized titanium wires (values in parentheses are estimated)

Sample no.	$\rho_{298}/\rho_{4.2}$ (=RRR)	ρ_{298}/ρ_{77}	$\rho_{4.2}$ (nΩm)	Oxygen conc. (mass ppm)	Nitrogen conc. (mass ppm)	H_V (kgf mm^{-2})
B1 (as received)	26.8	7.52	17.0	130	10	224
16-B1	98.6	10.0	4.52	28	43	89.2
17-B1	97.5	9.92	4.58	17	34	85.0
19-B1	94.7	9.92	4.72	22	45	92.5
24-B1[b]	27.3	7.78	17.1	500	53	125
B2 (as received)	24.4	7.39	19[a]	130	10	–
16-B2	62.0	9.28	7.7[a]	34	65	–
17-B2	(53)	9.12	(8.2)	(20)	–	–
19-B2	59.7	9.10	7.5[a]	27	92	–
24-B2[b]	23.9	7.48	20[a]	482	83	–
A (as received)	88.8	9.60	4.9[a]	110	5	131
4-A	101	9.90	4.5[a]	86	63	90.1
5-A	119	10.2	3.9[a]	37	48	85.7
6-A	111	10.1	4.1[a]	94	53	90.2
C (as received)	43.1	8.54	11[a]	150	10	185
3-C	122	10.1	3.6[a]	62	86	81.9
3-D	106	9.82	4.1[a]	61	63	81.9
F (as received)	9.28	5.10	54[a]	900	100	201
3-F	17.1	6.85	27[a]	80	100	103
24-F[b]	11.5	5.74	42[a]	(500)	–	132
F-anneal[c]	(9.1)	5.09	(54)	990	90	154

[a] Includes large error due to size measurement.
[b] Heat treated by using Ca–CaO equilibrium.
[c] Annealed in silica tube at 1273 K for 130 ks.

hardness. The resistivity ratios (RRR), $\rho_{298}/\rho_{4.2}$ and ρ_{298}/ρ_{77}, listed in Table 4 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 100 after deoxidation (*e.g.* nos. 4, 5 and 6-A), while that for commercial grade titanium wire showed only about 17 (no. 3-F).

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

$$\rho_T = \rho_{i,\,T} + \rho_0 + \Delta_{T,\,C} \tag{3}$$

where $\rho_{i,\,T}$ is the "ideal resistivity" arising from 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 4.2 K, $\rho_{4.2}$, in the case of titanium because $\rho_{i,\,T} + \Delta_{T,\,C}$ is negligible compared with ρ_0 at 4.2 K.

Assuming that Matthiessen's rule can be applied, that is, $\Delta_{T,\,C}$ in eqn. (3) is zero, values measurable with a high degree of accuracy can be expressed as follows:

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

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

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

$$\rho_{77}/\rho_{298} = A \times \rho_{4.2}/\rho_{298} + B \tag{6}$$

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 eqn. 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 eqn. (6), even though the ρ_0 of these samples may be very large. In addition, 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 (*i.e.* ρ_0 approaches 0).

In Fig. 4 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 in 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 eqn. (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 (eqn. (7)) A and B were calculated using the least-square approximation, and are depicted by the solid line in Fig. 4:

$$\rho_{77}/\rho_{298} = 0.951 \times \rho_{4.2}/\rho_{298} + 0.0918 \tag{7}$$

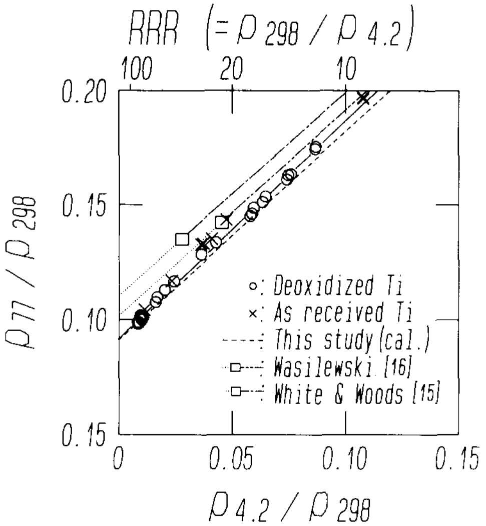


Fig. 4. Relationship between ρ_{77}/ρ_{298} and $\rho_{4.2}/\rho_{298}$ for deoxidized titanium wires. The dashed line is calculated on the basis of the results of deoxidized high-purity titanium (RRR ≑ 100) obtained in this study.

The sum of A and B in eqn. (6) should theoretically be one, whereas the measured value in eqn. (6) is 1.04. This 4% discrepancy is somewhat large and cannot be attributed solely to experimental error; it seems to be due to the 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 precise investigation of DMR, titanium purified further to a lower ρ_0 value is needed [13], and the effect of hydrogen on resistivity must also be considered [14].

3.5. Influence of oxygen on electrical resistivity

The residual resistivity, $\rho_{4.2}$, listed in the fourth column of Table 4, probably includes significant experimental error. All deoxidized wires were slightly etched by the salt and acid treatment, and except for sample B1, were too thin or short for accurate size measurement. The dimensions of sample B1, *e.g.* 80 mm (length) by 1.8 mm (mean diameter), were measured fairly accurately, unlike the other samples. The resistivity of this wire, which includes a maximum error of 5% due to size measurements, is, therefore, adopted in the following discussion.

In Table 5, the ideal resistivities at 77 and 298 K were calculated by using sample nos. 16, 17 and 19-B1 (see Table 4) on the assumption that $\Delta_{T,\,C}$ in eqn. (3) is negligible for samples with RRR of about 100. The data obtained by White and Woods [15] and by Wasilewski [16] are also listed for comparison. By using the values in Table 5, the constants A and B in eqn. (6) can be calculated. Calculated relationships between ρ_{77}/ρ_{298} and $\rho_{4.2}/\rho_{298}$ are illustrated in Fig. 4, along with their respective literature values

TABLE 5

Ideal resistivity of titanium at 298 and 77 K

	$\rho_{i,\,298}$ (nΩm)	$\rho_{i,\,77}$ (nΩm)	ρ_0 (nΩm)	Additional information
White and Woods [15]	437[a]	44.5[b]	19.7	$\rho_{i,\,273}=390$ nΩm
Wasilewski [16]	461[b]	50.9	13.1	$\rho_{i,\,273}=414$ nΩm
G. Elssner *et al.* [11]	430			210 ppm O, 20 ppm N
This study	440	40	4.6	30 ppm O, 50 ppm N

[a] Extrapolated.
[b] Interpolated.

TABLE 6

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)$^{-1}$)	T (K)	ρ_T (nΩm)	Oxygen conc. range (mol.% O)
Ames and McQuillan [17]	113	293	470	1.5
Wasilewski [18]	123	273	427	0.130–10.0
Elssner *et al.* [11]	82	298	430	0.063–1.0
Komatsu *et al.* [19]	101	77	60.6	0.890–3.2
Baur and Lehr [12]	103	20.4	2.68	0.009–0.32
This study	88	4.2	4.60	0.009–0.15

(□). The dashed line in Fig. 4 is calculated using the values in Table 5 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 eqn. (3) using a sample with large ρ_0, it is unavoidable that there is contribution of $\Delta_{T,\,C}$ to $\rho_{i,\,T}$. It therefore seems necessary to use as low a residual resistivity as possible to minimize the interference by DMR in the determination of the ideal resistivity.

The contribution by oxygen to the resistivity of titanium, $\Delta\rho/c$, determined in this study, as well as from the literature, is given in Table 6 [11, 12, 17–19]. The calculated value, 88 nΩm (mol.% O)$^{-1}$, using the data for samples B1 in Table 4, which contained 28, 17, 22 and 500 mass ppm oxygen is in fairly good agreement with the reported data. It is worth noting that the values of $\Delta\rho/c$ calculated from the data for samples B2 and F in Table 4 are 92 and 100 nΩm (mol.% O)$^{-1}$ respectively.

As indicated by Aleksandrov [20], it is better to measure the resistivity at temperatures as low as possible in order to avoid introducing an additional error due to DMR into the desired $\Delta\rho/c$ value. For this reason the value obtained in this study is believed reliable, but it should be noted that the range of oxygen concentrations in this study is rather limited, and the values themselves include some uncertainty.

4. Conclusion

Titanium in the form of wires and small pieces was deoxidized to a level of 20–60 mass ppm oxygen by use of Ca–$CaCl_2$ flux at 1273 K. The micro Vickers hardness value of electrolytically refined titanium was 80–90 kg mm^{-2} following deoxidation. The calcium, chromium, iron and nickel concentrations in titanium remained unchanged whereas impurities such as copper and silicon increased following deoxidation.

Resistivity measurements were carried out at 4.2, 77 and 298 K 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 ($\rho_{298}/\rho_{4.2} \fallingdotseq 100$) was produced, and the ideal resistivities at 77 and 298 K were determined to be 40 and 440 nΩm respectively. The contribution of oxygen to resistivity at 4.2 K was also measured by using titanium samples containing 30 and 500 mass ppm O, and determined to be 88 nΩm (mol.% O)$^{-1}$.

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