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Electrical Resistivities of Monocrystalline and Polycrystalline TiB_2

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The electrical resistivity of monocrystalline and polycrystalline TiB_2 was measured under an inert atmosphere by a four-point ac impedance technique over the range 298 to 1373 K. The results are expressed in the form $\rho - \rho_{298} = m(T - 298)$. The following values of ρ_{298} ($\mu\Omega \cdot$cm) and m ($n\Omega \cdot cm \cdot K^{-1}$) were determined: for polycrystalline TiB_2 (69% dense) 18.2 and 95; for polycrystalline TiB_2 (99% dense) 7.4 and 42; and for monocrystalline TiB_2 6.6 and 34.9.

I. Introduction

THE borides and carbides of many of the refractory metals are suitable for use as inert cathodes in molten salt electrolysis cells because they have high melting points, are electronic conductors, are wetted by molten metal, and resist chemical attack by molten metal and molten halides. To the detriment of their suitability for this use, these compounds are generally brittle, offer poor thermal shock resistance, and are subject to stress corrosion cracking, properties that can be improved by innovative materials processing techniques. As part of an investigation of candidate inert electrode materials for aluminum electrolysis in Hall cells, the electrical properties of polycrystalline and monocrystalline TiB_2 have been measured over the temperature range 25° to 1100°C.

Titanium diboride has been proposed for use as a structural element in Hall cells,[1] as a cathode material in chloride cells,[2] and as a cathode material in Hall cells.[3,4] Investigators have observed that the performance of TiB_2 in such applications is strongly dependent on porosity and on the presence of a second phase.[5,6] In the present study, the electrical conductivity of TiB_2 has been measured as a function of temperature, porosity, and phase composition. In particular this is the first report of the temperature dependence of the electrical resistivity of monocrystalline TiB_2 at elevated temperatures spanning those at which Hall cells operate.

Room-temperature resistivity values for TiB_2 single crystals have been reported. George *et al.*[7] made single crystals of TiB_2 and ZrB_2 by the Czochralski technique. Their matchstick-sized crystals were 99% pure, containing carbon and iron as the principal impurities. The resistivity of the TiB_2 crystal was reported to be 114 $\mu\Omega \cdot$cm at room temperature. Considerable evaporation of boron was observed during the crystal pulling. A more systematic study has been conducted in which the specimens were monocrystalline boules prepared by a modified Verneuil process using an electric arc.[8] The test crystals were 13 mm in length and 7 mm in diameter, having a purity of 99.7 wt%. The resistivities of eight different crystals at 20°C were measured by a Kelvin bridge to give a value of 6.6 ±0.2 $\mu\Omega \cdot$cm, independent of the orientation of the crystal. Values of 6 to 8 $\mu\Omega \cdot$cm at 22°C for 10 mm long by 7 mm diameter single crystals have been reported in a recent patent.[9]

Resistivity measurements for polycrystalline TiB_2 samples are more common in the literature, as the samples are relatively easy to prepare. Several papers report resistivities only at room temperature.[8,10–14] These results are summarized in Table I. The resistivities of specimens having a density greater than 90% lie between about 9 and 15 $\mu\Omega \cdot$cm. The measurement reported by Moers[10] in 1931 is probably the earliest. While Samsonov[12] does not state the formula used for the extrapolation of his results to 100% density, an equation of the form

$$\rho = \rho_0 \exp [A/(1 - P)] \quad (1)$$

where P is the fractional porosity, was probably used.[15] Juretschke and Steinitz[13] note considerable scatter in their results within and between different lots of TiB_2. They used an equation of the form

$$\rho = \rho_0 (1 - P)^n \quad (2)$$

to extrapolate the value of ρ_0. They found n to be −3.4. Chemical analyses and measurement methods are not reported in most of these papers.

Measurements of the electrical resistivity of polycrystalline samples of TiB_2 as a function of temperature[16–21] have been reproduced in Fig. 1. The lines were determined in the present study by linear regression analyses of the data reported in Refs. 16 to 21. The results are included in Table IV. Glaser and Moskowitz[16] report

Table I. Reported Values of Resistivity of Polycrystalline TiB_2 at Room Temperature

Ref.	Density (% of theor.)	Resistivity ($\mu\Omega \cdot$cm)	Comments
8	97	9.0 ± 0.1	Three samples measured
10	High	15.2	Coarse polycrystalline sample prepared by vapor deposition
11	85	26.5	Powder prepared by fused salt electrolysis and sintered
12	100	14.1*	Measured 5–10 specimens, densities 88–99%, prepared by hot-pressing
13	100	8.7*	Many samples; resistivity varied from 45 $\mu\Omega \cdot$cm at 60% density to 15 at 92%
14	High	14.4	No details given

*Extrapolated.

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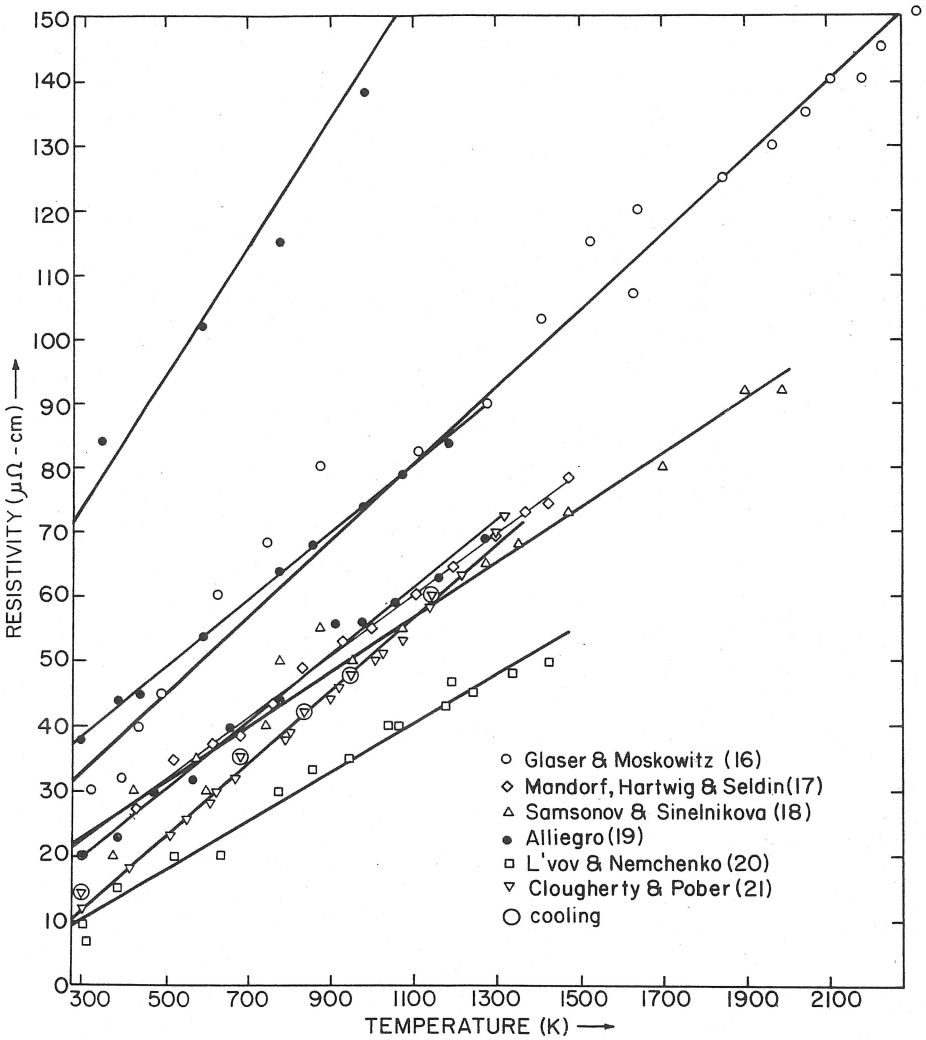

Fig. 1. Literature values for electrical resistivity of polycrystalline TiB_2.

Table II. Characteristics of TiB_2 Specimens

Characteristic	Polycrystalline samples 1 and 2*	Polycrystalline sample 3†	Single-crystal sample 3
Chemical composition (wt%)			
Ti	68.6	68.0	70.0
B	30.9	30.2	30.1
C	0.37	0.77	
O		0.0068	
Fe	0.1	0.01	
Ti + B	99.5	98.2	100.1
Stoichiometry of TiB_x (mol B/mol Ti)	2.00	1.97	1.91
Grain size (μm)	<45	4	
Density (% theor.)	69	99	100

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Table III. Orientation of Crystal Axis in Monocrystalline TiB_2 Specimens

Single-crystal specimen No.	Orientation of growth axis with respect to low-index planes (deg) (100)	(110)	(001)	Crystal length (cm)
	30	17.5	73.5	3
1	15.5	14.5	90	
2	39	31.5	59	5
3	16.5	13.5	90	1.5

measurements made up to a temperature of 2030°C. The sample was self heated by the passage of current under an inert atmosphere. The voltage drop was used to calculate the resistance and a pyrometer was used to measure temperature. Mandorf *et al.*[17] passed a dc current through their externally heated samples and measured the resulting voltage drop. Their temperature-dependence results were reported for a sample having a relative density of 77%. Six samples of varying porosity were used to establish a relationship between porosity and room-temperature resistivity. The results fit Eq. (2) with a value for n of -3 and 9.1 $\mu\Omega\cdot$cm for ρ_0. Samsonov and Sinelnikova[18] used a similar technique to that of Ref. 16 to make measurements up to 1710°C. Alliegro[19] reports temperature-dependence results for three different samples: sintered, 66% dense; hot-pressed, 93% dense; and modified hot-pressed, 93% dense. Measurements were made using a four-point contacting arrangement. L'vov and Nemchenko[20] state that their measurements were made using a compensation bridge with the sample under vacuum. The results of Clougherty and Pober[21] show less scatter due to their use of the four-point measurement technique. Samples having a relative density of 96% and a purity of 99.8% were prepared by hot-pressing at 1950°C. Samsonov and Grebenkina[22] report temperature dependence by giving the resistivity at 970 K as well as a temperature coefficient without any experimental details. They used an equation of the form

$$\rho = \rho_0[2/(2 - 3P)] \quad (3)$$

to convert their resistivity values to 100% density. Their results have been transformed so they could be included in Table IV. The results of Aivazov and Domashnev[23] have not been included as they are nearly an order of magnitude higher than all other reported values.

Table IV. Electrical Resistivity of Polycrystalline and Monocrystalline TiB_2

Specimen	Number of data points	ρ_{298}, interpolated resistivity at 298 K ($\mu\Omega\cdot$cm)	m, gradient in resistivity (n$\Omega\cdot$cm/K)	α, average coefficient of resistivity (mK^{-1})
		Present study		
Polycrystal 1	19	18.4 ± 0.5	94.3 ± 0.7	5.1 ± 0.2
Polycrystal 2	25	18.0 ± 0.4	96.9 ± 0.7	5.4 ± 0.2
Polycrystal 3	23	7.4 ± 0.2	42.2 ± 0.4	5.7 ± 0.2
"Single"-crystal 1*	22	9.0 ± 0.4	43.0 ± 0.6	4.8 ± 0.3
Single-crystal 2	22	6.6 ± 0.2	34.5 ± 0.3	5.2 ± 0.2
Single-crystal 3	24	6.7 ± 0.2	35.2 ± 0.3	5.3 ± 0.2
		Literature values		
Ref. 16	21	33 ± 2	60 ± 2	1.8 ± 0.2
Ref. 17	14	22.5 ± 0.7	47 ± 1	2.1 ± 0.1
Ref. 18	16	23 ± 2	43 ± 2	1.9 ± 0.2
Ref. 19 (sintered)	6	74 ± 4	100 ± 6	1.4 ± 0.1
Ref. 19 (hot-pressed)	11	20 ± 1	52 ± 2	2.6 ± 0.2
Ref. 19 (modified hot-pressed)	10	38.5 ± 0.4	53 ± 1	1.4 ± 0.1
Ref. 20	15	10 ± 1	38 ± 1.5	3.8 ± 0.5
Ref. 21	23	11.4 ± 0.6	56 ± 1	5.0 ± 0.3
Ref. 22	?	15	31	2.0

*Proved to be a bicrystal.

Resistivity values from the literature as well as those from the present study were fit to an equation of the form

$$\rho - \rho_{298} = m(T - 298) \quad (4)$$

where ρ is resistivity in $\Omega\cdot$cm, T is temperature in K, and m is the average gradient in resistivity over the temperature interval of the data. Also given in Table IV is α, the average coefficient of resistivity, defined as

$$\alpha = m/\rho_{298} \quad (5)$$

where m and ρ_{298} are defined in Eq. 4. Clougherty and Pober[21] have suggested that α is a measure of the intrinsic electrical behavior of a material.

II. Experimental Procedure

The conductivity of TiB_2 is as high as that of many metals, and in fact higher than that of titanium metal itself. Thus, the optimum specimen geometry for electrical conductivity measurements is cylindrical with maximum length-to-diameter ratio.

The polycrystalline samples used in this study were cut from plates to a size of about 0.16 by 0.16 by 8 cm. The chemical analyses and densities as reported by the supplier are given in Table II.

To prepare single crystals, Cerac* material (see Table II) was used as the feed to a crystal growth apparatus[24] based upon the floating zone melting technique. The concentrated beam of a 1-kW CO_2 laser heats the feed material to its melting point, about 2900°C, to produce single crystals about 0.5 mm in diameter and 6 cm long. While the crystals were mostly covered by a thin layer of black material, probably condensed TiB_2, a freshly cleaved surface showed a typical metallic luster. Table II contains the results of the chemical analysis of single-crystal sample 3 for Ti and B. The crystal was dissolved in a solution containing 33 vol% nitric acid and 33 vol% hydrofluoric acid in water. Ti and B were analyzed by plasma emission spectroscopy. To check for the presence of second phase, cross sections of single-crystal sample 1 were subjected to microscopic examination. These samples were mounted, ground, and diamond polished to a mirror finish. They were etched for 30 s in a solution of 4 vol% hydrofluoric acid, 13 vol% hydrochloric acid and 42 vol% nitric acid in glycerine. The presence of second phase was undetectable on examination with both optical and scanning electron microscopes. During crystal growth approximately 30% of the feed material was lost by evaporation. X-ray diffraction analysis of the powder coating the growth chamber showed it to be TiB_2.

Table III gives the orientation of the axis of each of the single crystals as determined by Laué back reflection. Laué patterns were also taken at various sites along the length of the crystal. The results confirmed that the second and third crystals, denoted as single-crystal samples 2 and 3, have no grain boundaries between the voltage probe locations, while the first crystal, single-crystal sample 1, had one grain boundary. While the crystals were symmetrical along their axes, their radii varied along their lengths due to fluctuations in the density of the feed rods. The effective diameters were determined by the use of an image analyzer and confirmed by micrometer measurements.

Specimens were heated in an electrical resistance furnace under an inert atmosphere of argon which was passed over hot titanium sponge. The electrical resistance of the specimens was measured by a variable frequency LRC testing device† using the four-point ac impedance technique. Test frequency was set at 234 Hz following a preliminary study which detected no change in the measured impedance over the range 234 Hz to 20 kHz. As the single-crystal specimens were extremely fragile, electrical contact between the specimen and the lead wires could not be made using pressure connections such as those described in Ref. 21. Instead, fine platinum wires, 0.2 mm in diameter, were wrapped around the specimen. The temperature of the specimen was measured by an ASTM type R, Pt–13% Rh vs Pt, thermocouple whose tip touched the specimen at midlength. Table IV and Fig. 2 display the results measured in the present study. All error estimates are those derived from regression analysis.

III. Discussion

Resistivity results at room temperature will be considered first. It can be seen that the single-crystal value of 6.7 ± 0.2 $\mu\Omega\cdot$cm for the two crystals measured is in excellent agreement with the results of Mersol *et al.*[8] of 6.6 ± 0.2 $\mu\Omega\cdot$cm. The value of 114 $\mu\Omega\cdot$cm reported by George *et al.*[7] is far too high. As expected, resistivity increases with porosity, as can be seen from the results taken from the polycrystalline samples. The value of 7.4 ± 0.2 $\mu\Omega\cdot$cm for the high-density specimen, polycrystalline sample 3, is somewhat lower than other values reported for high-density material. However, polycrystalline sample 3 has an uncommonly high density of 99%. It is difficult to assess the extrapolated values of Samsonov[12] and Juretschke and Steinitz,[13] since there is no agreement on a mathematical expression for the variation of resistivity with porosity.

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†Model 1688 Digibridge, GenRad, Concord, MA 01742.

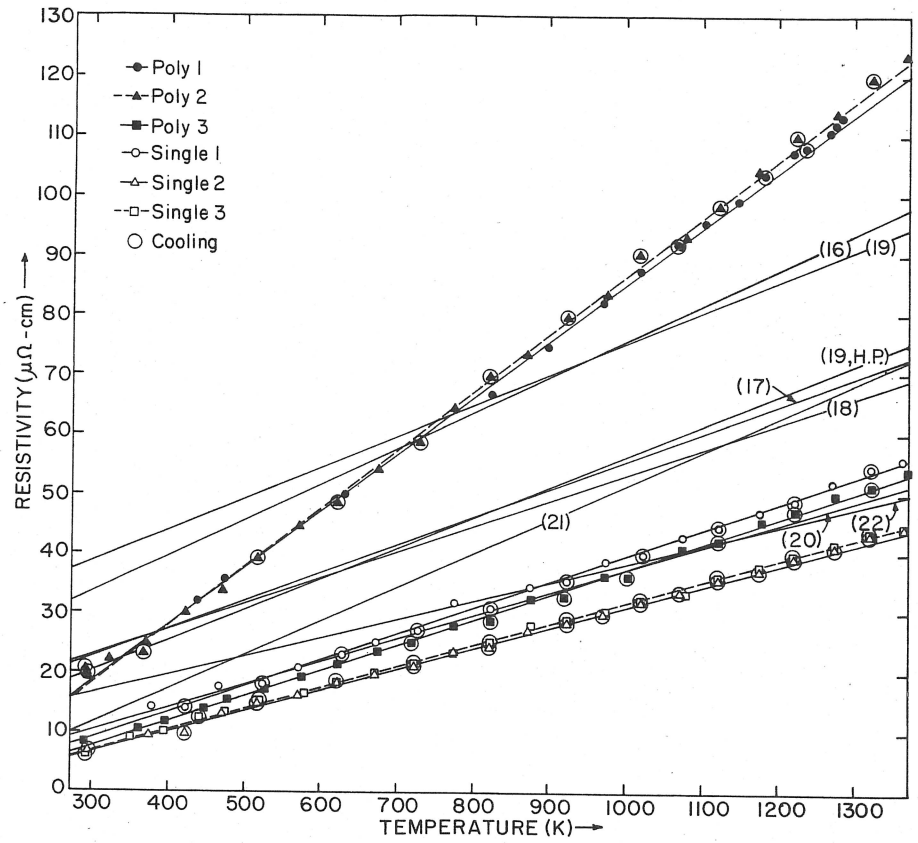

Fig. 2. Electrical resistivity of polycrystalline and monocrystalline TiB_2.

The metallic nature of the electronic structure of TiB_2 is readily apparent from Fig. 2. The resistance of a metal of a given composition is due only to the thermally induced lattice vibrations. This should lead to a resistance that increases linearly with temperature, as seen in Fig. 2.

Table IV reveals several trends. The slope decreases with decreasing porosity, as does the resistivity at 298 K. It has been argued that the average coefficient of resistivity, α, should be independent of sample porosity.[21] For Cerac[1] derived material α has the value of 5.2 ± 0.2 mK^{-1} regardless of whether it is monocrystalline or polycrystalline. This value is in agreement with the measurements of Clougherty and Pober.[21] The PPG‡ material has a somewhat higher α, and other reported values are lower. The data in Refs. 16 to 18 and 22 yield α values of about 2.0 mK^{-1}.

The scatter in the data reported in Refs. 16 and 18 is high, especially at lower temperatures. This is probably due to the fact that the current used to heat the specimen was also used in the resistance measurement. The data of L'vov and Nemchenko[20] also show scatter; however, our calculation of the least-squares line of their measurements agrees well with the resistivities of the high-density polycrystalline specimens measured in the present work. The results of Clougherty and Pober for a 96% dense specimen lie between those measured herein for specimens having densities of 69 and 99%. The resistivity of the bicrystal, single-crystal sample 1, is greater than that of the two single crystals, single-crystal samples 2 and 3. The increase of resistivity of the bicrystal could be due to the presence of the grain boundary.

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