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Electrical resistivities in single crystals of TiC_x and VC_x

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TiC_x and VC_x have wide non-stoichiometric composition ranges which come only from the carbon vacancies. High purity single crystals with controlled compositions were prepared, and their electrical resistivities at 4.2 and 298 K were measured as a function of composition. In the case of TiC_x whose carbon vacancies are disordered in the lattice, the dependence of the residual resistivity on the composition was interpreted by applying Nordheim's rule to the vacancy scattering and by considering the change in carrier density due to the introduction of vacancies. In addition, the difference in the resistivity between 4.2 and 298 K was discussed. In the case of VC_x whose carbon vacancies are ordered, the dependence of the resistivity on the composition ranges of the ordered phases was examined in detail.

1. Introduction

The IVa and Va groups of transition metal carbides have a NaCl-type crystal structure and many characteristic properties such as high melting points (> 2650° C), great hardness (> 2400 kg mm^{-2}) and metallic properties [1]. We are interested in their fundamental properties, and have already reported on them [2–5]. In this paper, we report on the electrical resistivity of the carbides. The resistivity has already been measured by many investigators [1], but the data varies from sample to sample. The difference in the measured values can usually be attributed to the following factors [1]: (a) the composition of the sample which comes only from the carbon vacancies; and (b) the content of impurities, such as oxygen and nitrogen.

Therefore, in this paper, TiC_x whose carbon vacancies are disordered in the lattice and VC_x whose vacancies are ordered are selected, and their high purity single crystals with controlled compositions were prepared by the radiofrequency (RF) zone levelling floating zone technique. The electrical resistivities are measured at 4.2 and 298 K. The dependence of the residual resistivity on the composition and the difference in the resistivity between at 4.2 and 298 K are discussed.

2. Experimental details

The single crystals of TiC_x and VC_x were prepared at several atmospheres of ambient helium gas by the RF floating zone technique. The size of the crystal rods was about 6 cm long and 9 mm in diameter. The composition of grown crystals was controlled by keeping the molten zone composition to be the liquidus composition which coexists with a desired crystal composition (the solidus composition) using a modified zone levelling method [6]. The single crystals of TiC_x were prepared in the composition range higher than C/Ti = 0.7. The single crystals of VC_x were prepared over the entire composition range (0.7 < C/V < 0.88). The contents of oxygen and nitrogen impurities in their crystals were less than a few hundred p.p.m., respectively. The preparation and characterization of these crystals has been described in detail [6–8].

Samples for measurements were cut out of the single crystal rods using a spark corrosion cutter. The rectangular samples which consisted of the (1 0 0) planes were etched briefly in a mixture of hydrofluoric and nitric acids at room temperature, and then washed in an ultrasonic bath to remove the surface residue. The size of samples was about 1 mm × 1 mm × 8 mm. All resistivity measurements were performed at 4.2 and 298 K using a four-probe d.c. technique. Electrical currents flowed along the $\langle 1 0 0 \rangle$ axis. The uncertainty of measured resistivity was estimated to be ± 5%, which was caused mainly by the uncertainty of distance between the potential probes.

3. Results and discussion

3.1. TiC_x

TiC_x has a wide non-stoichiometric composition range which comes only from the carbon vacancies. In order to eliminate the scattering of conduction electrons by phonons and observe that only by the vacancies, the resistivity of single crystal TiC_x was measured at 4.2 K. The residual resistivity at 4.2 K is shown in Fig. 1. $TiC_{0.75-0.8}$ has the maximum resistivity of $210 \times 10^{-8}\,\Omega m$. With decreasing the vacancy content, the resistivity decreases. The residual resistivity of stoichiometric TiC is estimated by extrapolation to be zero, which shows that the conduction electrons are scattered only by the carbon vacancies and indicates that the scatterings are not due to impurities or other imperfections in the crystal.

The dependence of the residual resistivity on the composition (vacancy content) can be explained as follows. The electrical resistivity is proportional to

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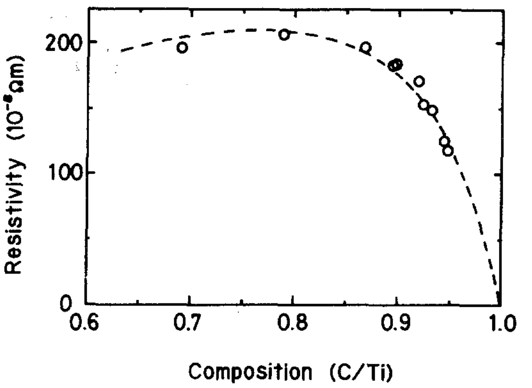

Figure 1 Residual resistivity of single-crystal TiC$_x$ as a function of compositon. The circles show the measured values. The dashed line is derived from the equation $\varrho_{4.2}(x) \propto x(1 - x)/[0.1 + (1 - x)]$.

$m/n\tau_v$, where m is an effective mass, n is a carrier density and τ_v is the relaxation time due to the carbon vacancies. The reciprocal relaxation time $(1/\tau_v)$, that is, the amount of scattering for unit time, was thought to be proportional not to the vacancy content $(1 - x)$, but to $x(1 - x)$ by applying Nordheim's rule [9], which is applied in the two component alloy system, because the vacancy content is very high in the carbides. In addition, the dependence of the carrier density on the composition can be thought to be $n_0 + (1 - x)$. Here, n_0 is a number of conduction electrons in the presumed stoichiometric TiC. The latter term comes from the fact that, according to recent calculation of band structure [10], the number of conduction electron per unit formula increases by the vacancy content $(1 - x)$ in the non-stoichiometric carbides. Here, we assume that the effective mass is almost independent of the composition, which is a reasonable assumption in the present case. After all, the following equation could be obtained

$$\varrho_{4.2} \propto \frac{x(1 - x)}{n_0 + (1 - x)} \tag{1}$$

Here, a proportionality constant corresponds to the product of the effective electron mass and the scattering probability of the vacancy. Equation 1 was fitted to the experimental data by the least-squares method. The proportionality constant was found to be 392, and n_0 was found to be 0.1 which is consistent with William's data [11]. The calculated curve is shown as a dashed line in Fig. 1. The measured values and the dashed line agree well as expected. Therefore, the residual resistivity of TiC$_x$ could be explained from both the scattering of conduction electrons by the carbon vacancies and the change in carrier density due to the introduction of carbon vacancies.

Fig. 2 shows the electrical resistivity of TiC$_x$ at 298 K, and the difference $(\Delta\varrho)$ in resistivity between 4.2 and 298 K. The difference in resistivity $(\Delta\varrho)$ becomes smaller as the composition deviates from the stoichiometry. When 15% of the carbon vacancies are introduced, that is, the composition is C/Ti = 0.85, the difference becomes almost zero. In the lower composition range, the difference increases a little. The temperature coefficient $(\mathrm{d}\varrho/\mathrm{d}T)$ of resistivity has already been discussed by Williams [12]. He concluded

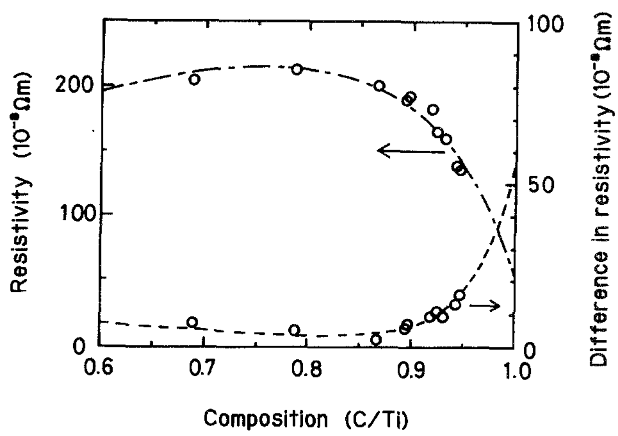

Figure 2 Electrical resistivity of single-crystal TiC$_x$ as a function of composition at 298 K, and the diffusion in resistivity betwen at 4.2 and 298 K.

that the temperature coefficient of resistivity is proportional to the Hall coefficient, with assumptions that the Hall coefficient is independent of temperature and that the mobility is inversely proportional to temperature. In the case of $\mathrm{d}\varrho/\mathrm{d}t = 0$, which can not be explained according to his interpretation, he insisted that the Hall coefficient changes so as to make the temperature coefficient of resistivity zero. Further information can not be obtained from his analysis. Therefore, we analysed the difference in resistivity between at 4.2 and 298 K as follows. The resistivity at 298 K arises from the scattering by the carbon vacancies and phonons. It is known from the measurement of the Hall coefficient that increasing the temperature tends to increase the carrier density if a single-carrier model is appropriate [1, 11, 12]. Therefore, the difference resistivity can be interpreted as follows

$$\begin{aligned} \Delta\varrho(x) &\equiv \varrho_{298} - \varrho_{4.2} \\ &= A\left[\frac{(1/\tau_v) + (1/\tau_p)}{n + \Delta n} - \frac{(1/\tau_v)}{n}\right] \\ &= \left(\frac{A}{n + \Delta n}\right)\left[(1/\tau_p) - \frac{\Delta n}{n}(1/\tau_v)\right] \end{aligned} \tag{2}$$

where A is a proportionality constant which corresponds to the effective electron mass, τ_p is the relaxation time due to phonons and Δn is the change in carrier density due to the temperature increase up to 298 K. The first term represents the resistivity increase due to phonon scatterings. The second term represents the decrease of resistivity by vacancy scattering due to the increase of carrier density. In the non-stoichiometric TiC$_x$, the second term becomes large because the scattering number $(1/\tau_v)$ due to the vacancies is large, and consequently the difference resistivity $(\Delta\varrho)$ between at 4.2 and 298 K becomes small. Thus Equation 2 explains well the experimental data qualitatively. The temperature coefficient of the resistivity becomes zero, when $[(1/\tau_p)/(1/\tau_v)] = \Delta n/n$. In addition, we tried to fit Equation 2 to the experimental data with assumptions that $1/\tau_p$ is independent of the composition, and that the change in carrier density is proportional to the composition $(\Delta n = \alpha x)$. The former assumption is reasonable, as a first approximation. The latter assumption is not so strange because

Δn comes from the transition between the bands near the Fermi level [13], and introducing the vacancies makes the Fermi level higher, and the change in the carrier density lower. The following equation is obtained from Equation 2

$$\Delta\varrho(x) = \frac{392}{0.1 + (1 - x) + \alpha x} \times \left\{B - \left[\frac{\alpha x}{0.1 + (1 - x)}\right][x(1 - x)]\right\} \qquad (3)$$

where B is the product of $(1/\tau_p)$ and $[x(1 - x)/(1/\tau_v)]$. The constants, B and α were determined to be 0.020 and 0.04, respectively, by the least-squares method. The fitted curve is shown as a dashed line in Fig. 2. The fitted curve shows the minimum value at the composition (C/Ti) of 0.8 to 0.85, and agrees well with the experimental data. The dash-dotted line in Fig. 2 shows the resistivity at 298 K obtained from Equations 1 and 3 ($\varrho_{298} = \varrho_{4.2} + \Delta\varrho$). As a matter of course, the dash-dotted line agrees well with the resistivity measured at 298 K. The stoichiometric TiC has the resistivity of $56 \times 10^{-8}\,\Omega$m at 298 K. Furthermore, the contribution of vacancy and phonon scattering to the resistivity at 298 K was calculated from the obtained values of B and $x(1 - x)$. The contribution of phonon scatterings was found to be 30, 20 and 10% at the composition (C/Ti) of 0.95, 0.9 and < 0.8, respectively. It was confirmed that the resistivity at 298 K is almost determined by the vacancy scattering.

3.2. VC_x

Table I shows the resistivities of VC_x at 4.2 and 298 K. Fig. 3 shows the resistivity at 4.2 K as a function of composition. VC_x has two ordered phases, V_6C_5 and V_8C_7, in the composition range. Their composition ranges which were determined by X-ray powder diffraction [7] are also shown in Fig. 3. The dependence of the resistivity on the composition corresponds closely to the composition ranges of the ordered phases. If the disordered VC_x phase exists over the entire composition range, its resistivity can be said to be proportional to $x(1 - x)/[1 + (1 - x)]$ by applying Equation 1. Here, we assume that a stoichiometric VC has one conduction electron per formula because VC has one more valence electron than TiC. Using the resistivity ($139.4 \times 10^{-8}\,\Omega$m) of disordered $VC_{0.749}$, the proportionality constant was found to be 929. This value is reasonable, compared with the value of 392 in Equation 2, because it is expected that the conduction electron in VC has a heavier effective mass than that in TiC. This relation is shown as a dashed line in Fig. 3. In the composition range higher than C/V = 0.76, the resistivity rapidly decreases with decreasing vacancy content. Compared with the dashed line, the decrease of resistivity is interpreted to be due to vacancy ordering. The measured resistivities showed the lowest values at the ideal compositions, that is, $VC_{0.833}$ and $VC_{0.875}$, of the V_6C_5 and V_8C_7 phases. This shows that the carbon vacancies do not scatter the electron any longer because of the long range ordering. In the V_6C_5 phase, the sample of $VC_{0.835}$ showed the lowest residual resistivity of $27 \times 10^{-8}\,\Omega$m. If the sample with the ideal composition ($VC_{0.833}$) is prepared, the residual resistivity will decrease further. The lowest residual resistivity of the V_8C_7 phase was $1.7 \times 10^{-8}\,\Omega$m and its residual resistance ratio (*RRR*) was 18 ($30.7 \times 10^{-8}/ 1.7 \times 10^{-8}$). These values are the highest among the already reported values ($\varrho_{4.2} = 3.2 \times 10^{-8}\,\Omega$m, $RRR = 10$) [14]. In the V_6C_5 and V_8C_7 composition ranges, the change in resitivity per 1 at % of vacancy is smaller in the lower composition regions than the ideal compositions, compared with that in the higher composition regions, as shown in Table I. This can be easily understood from the fact that the vanadium sublattice is distorted by introducing carbon into the octahedral sites and then the ordered phases are formed [1] because VC_x has the smallest octahedral sites among the VIa and Va carbides. Therefore, taking off carbon from the ideal V_6C_5 and V_8C_7 does not increase the resitivity so much as putting carbon into them.

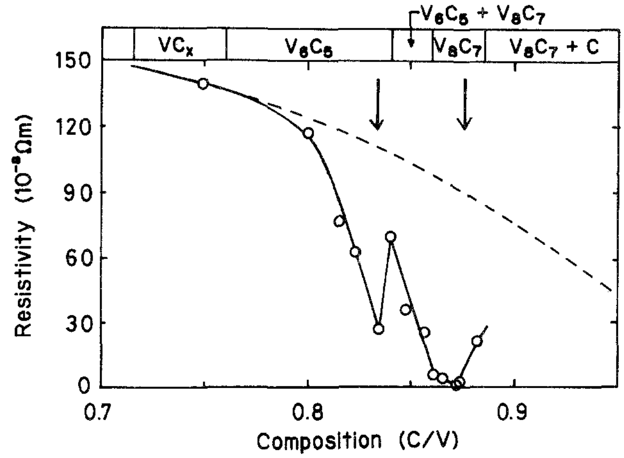

Figure 3 Electrical resistivity of single-crystal VC_x as a function of composition at 4.2 K, and the composition ranges of the ordered phases. The two arrows show the ideal compositions of V_8C_7 and V_6C_5 phases. The dashed line shows the presumed resistivity of disordered VC_x, which is derived from the equation $\varrho_{4.2}(x) \propto x(1 - x)/[1 + (1 - x)]$.

TABLE I Resistivity at 4.2 and 298 K, and resistivity at 4.2 K per at % for VC crystals of various C/V ratios

Compositon (C/V)	Phase	Resistivity ($10^{-8}\,\Omega$m)		$\frac{\varrho_{4.2}}{\Delta(C/V)^*}$
		ϱ_{298}	$\varrho_{4.2}$	
0.749	VC_x	142.1	139.4	–
0.800	V_6C_5	119.9	117.2	35.5
0.815		95.1	76.7	42.6
0.823		84.0	62.2	62.2
0.835		61.5	26.8	134
0.840		85.7	69.5	139
0.847	V_6C_5 $+V_8C_7$	78.0	35.8	–
0.857		63.0	26.3	–
0.861	V_8C_7	46.2	6.6	4.7
0.865		41.8	5.3	5.3
0.872		30.7	1.7	5.6
0.874		31.3	3.1	31
0.882		52.4	21.7	31

*The difference between the composition and the ideal compositions (C/V = 0.833 and 0.875) of ordered V_6C_5 and V_8C_7 phases, respectively.

A disordered $VC_{0.749}$ has the highest resistivity and its resistivities at 4.2 and 298 K were almost the same value because the vacancy content is high as already explained by Equation 2. At the ideal compositions of the ordered phases, the difference in resistivity between at 4.2 and 298 K becomes large. This is because the second term of Equation 2 becomes small.

4. Conclusions

The electrical resistivities of TiC_x and VC_x were measured at 4.2 and 298 K, using high purity single crystals with controlled compositions.

For TiC_x whose carbon vacancies are disordered, the dependence of the residual resistivity on the composition were explained by applying Nordheim's rule to the vacancy scattering and by considering the change in carrier density due to the introduction of carbon vacancies. In addition, the resistivity at 298 K was measured, and the difference in resistivity between at 4.2 and 298 K was discussed. The difference in resistivity was found to become small when the vacancy content is high and this is interpreted by carrier density increase with increasing the temperature.

For VC_x whose vacancies are ordered, the dependence of the resistivity on the composition corresponded closely to the composition ranges of the ordered phases. The lowest residual resistivity in the V_8C_7 phase was $1.7 \times 10^{-8}\,\Omega m$, which was the lowest value among the reported values. The residual resistivity will be become still lower by controlling the composition more strictly. If so, the Fermisurface measurement will be possible and the electronic structure and bonding characters of the carbides will be understood more clearly.

References

1. L. E. TOTH, in "Transition Metal Carbides and Nitrides" (Academic Press, New York, 1971) p. 4.
2. M. AONO, Y. HOU, R. SOUDA, C. OSHIMA, S. OTANI and Y. ISHIZAWA, *Phys. Rev. Lett.* **50** (1983) 1293.
3. C. OSHIMA, R. SOUDA, M. AONO, S. OTANI and Y. ISHIZAWA, *Phys. Rev.* **30** (1984) 5361.
4. R. SOUDA, M. AONO, C. OSHIMA, S. OTANI and Y. ISHIZAWA, *Surf. Sci.* **150** (1985) L59.
5. Y. ISHIZAWA and T. TANAKA, *Solid State Commun.* **51** (1984) 743.
6. S. OTANI, T. TANAKA and Y. ISHIZAWA, *J. Cryst. Growth* **61** (1983) 1.
7. Y. HOU, S. OTANI, T. TANAKA and Y. ISHIZAWA, *ibid.* **68** (1984) 733.
8. S. OTANI, T. TANAKA and Y. ISHIZAWA, *ibid.* **71** (1985) 615.
9. N. F. MOTT and H. JONES, in "The Theory of the Properties of Metals and Alloys" (Dover Publication, New York, 1958) p. 296.
10. B. M. KLEIN, D. A. PAPACONSTANTOPOULOS and L. L. BOYER, *Phys. Rev.* **B22** (1980) 1946.
11. W. S. WILLIAMS, *Phys. Rev.* **135** (1964) A505.
12. *Idem*, "Progress in Solid State Chemistry", Vol. 6 (Pergamon Press, Oxford, 1971) p. 57.
13. H. IHARA, Y. KUMASHIRO and A. ITOH, *Phys. Rev.* **B12** (1975) 5465.
14. L. W. SHACKLETTE and W. S. WILLIAMS, *ibid.* **B7** (1973) 5041.

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