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SUMMARY

The Hall coefficient within the entire cubic phase region of tantalum carbide was investigated by a direct-current method and was found to be negative and to increase in absolute magnitude with increasing carbon content, while the electrical resistivity was found to decrease. These results, as well as the known variation of the magnetic susceptibility and the superconductivity transition temperature with carbon content, indicate that a one-carrier model is not adequate to describe the entire system. A composition in the ditantalum carbide phase region was also found to have a negative Hall coefficient, its magnitude being greater than that of any of the other samples. Magnetoresistivities were too small to be accurately measured.

INTRODUCTION

A number of investigators (refs. 1 to 4) have measured the Hall coefficients of the group IV and V transition metal carbides and nitrides and their solid solutions having sodium chloride type crystal structure in order to understand more fully the electronic binding in these materials. Their samples have been restricted either to nearly stoichiometric compositions or to solid solutions of nearly stoichiometric components. The results of these investigations have been expressed in terms of the variation of the valence electron concentration (VEC), that is, the valence electrons per formula with the expressed or implied assumption that the electronic band structure is not strongly affected by differences in the ionic cores. A recent band structure calculation on titanium carbide (ref. 5), however, implies that substitutional alloying of either the metal or the nonmetal atom may significantly alter the density-of-states curve, even if the VEC is unchanged. The histograms of density of states for titanium carbide and titanium nitride as recently calculated by Ern and Switendick (ref. 6) clearly differ from each other not only with respect to the position of the Fermi level, but also with respect to the energy distribution of the density-of-states and to the degree of band interaction. Thus, the band

structure of one of these compounds cannot be universally employed for the others. These calculations, then, confirm the desirability of varying the VEC without resorting to substitutional alloying. Since these compounds exhibit rather wide single-phase regions, the VEC can be varied over a large range merely by changing the concentration of the nonmetal atom. Thus, in order to study more fully the effect of changes in the VEC on the electrical nature of tantalum carbide (TaC), room temperature Hall measurements were made on TaC ribbons of different carbon contents. The electrical resistivity of each specimen was also determined, and attempts were made to determine magnetoresistivity. Measurements were also made on a sample of the hexagonal carbide, Ta_2C. The data are discussed in relation to the band structure determinations which have appeared in the literature for the group IV and group V transition metal carbides and nitrides and in conjunction with other properties of nonstoichiometric tantalum carbide.

EXPERIMENTAL PROCEDURE

Tantalum carbide ribbons were prepared by heating pieces of tantalum foil (19 by 0.32 by 0.0025 cm) in measured amounts of propane for 6 hours at 2000° C. The purity of the tantalum was at least 99.89 percent. The method is similar to that used previously in the preparation of substoichiometric tantalum carbide filaments (ref. 7). An X-ray diffraction pattern was made on each of the specimens with a 114.6-millimeter-diameter Debye-Scherrer camera using copper $K\alpha$ radiation. The lattice parameters, a_o, were calculated by means of a least-square extrapolation on an IBM 7094 computer. With these data and an established literature curve of a_o against carbon content (ref. 8) the composition of each sample was ascertained. The estimated accuracy of the carbon determination using this procedure is about $TaC_{X\pm0.006}$.

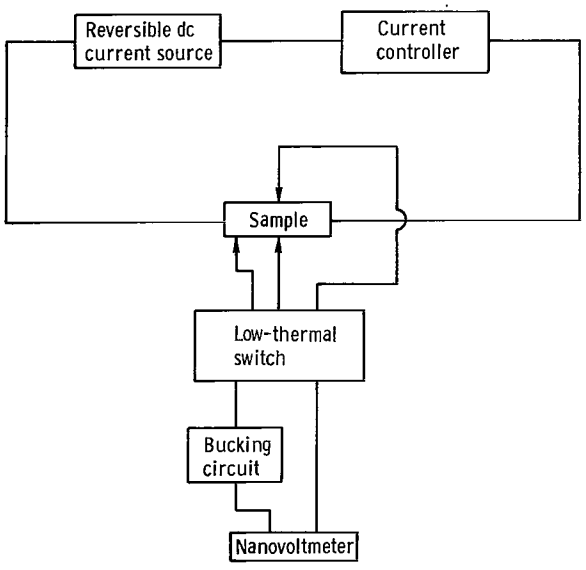


Figure 1. - Schematic of electrical circuit of Hall apparatus.

A 1.4-centimeter length from each carburized ribbon was used as the Hall specimen. A direct-current method was employed in the Hall measurements. The electrical circuit is shown in figure 1. All the vital circuit parts were electrically and magnetically shielded. The low thermal switch permitted the selection of the desired pair of leads while introducing thermal voltages of less than 10^{-9} volt. All stray voltages could be suppressed by the bucking

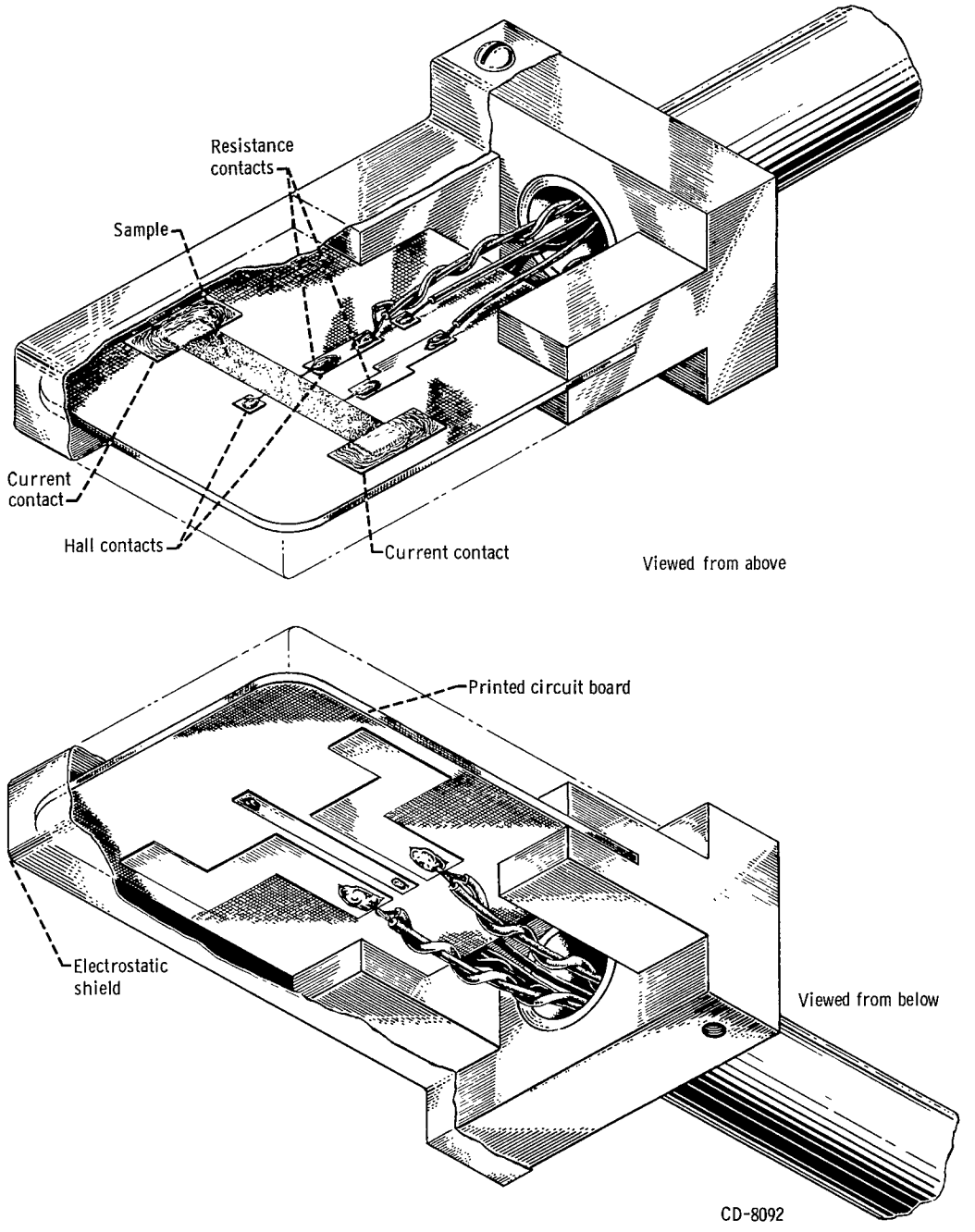


Figure 2. - Schematic of Hall probe.

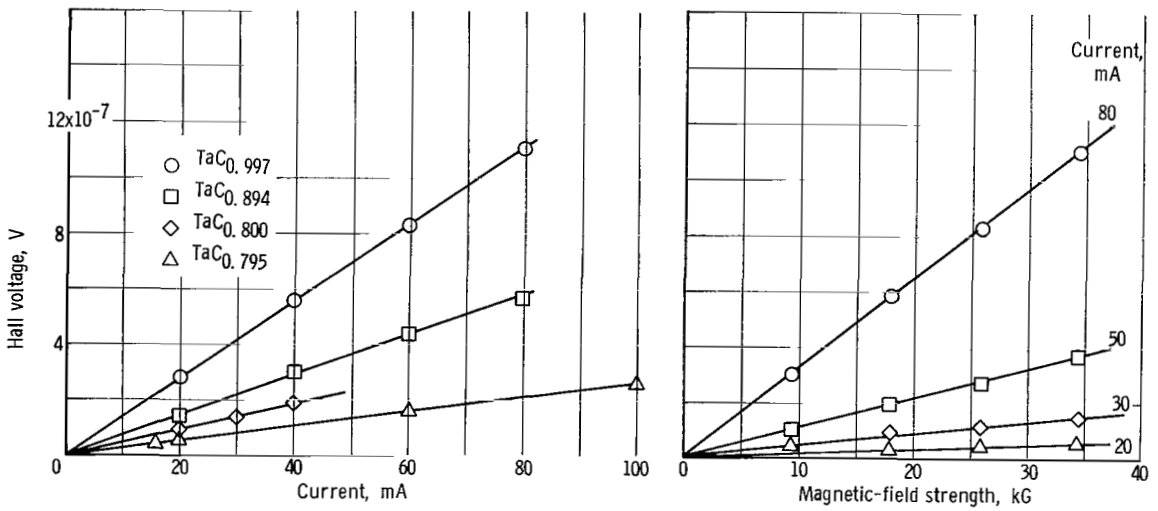
circuit to less than 10^{-9} volt. The voltage signal over a 10-minute interval was stable to within 10^{-9} volt.

A drawing of the probe head, which was 4.4 by 2.5 by 0.6 centimeter, is shown in figure 2. The printed circuit board provided a convenient way of minimizing circuit loops, which could otherwise produce stray voltages and fields. The leads were connected to the copper strips on the circuit board with solder that has a low thermoelectric effect with copper. The electrical contacts to the sample were provided by a liquid mercury-indium alloy to circumvent problems of wetting and generation of thermal stresses when other methods of soldering or welding were attempted.

Measurements were taken of the transverse voltage with reversal of both current and magnetic field. First the voltage was measured as a function of current (fig. 3(a)) at the highest magnetic field available. The linear variation in these curves indicated freedom from thermal gradients caused by excessive Joule heating (proportional to the current squared). Then a convenient current was chosen, and the transverse voltage was measured as a function of the magnetic field (fig. 3(b)). This procedure indicated the validity of the linear variation of the Hall voltage with the magnetic field as given in the Hall equation

$$E_H = \frac{RBI}{t} \times 10^{-8}$$

where



(a) Current; magnetic-field strength, 34.4 kilogauss.

(b) Magnetic-field strength.

Figure 3. - Variation of Hall voltage with current and magnetic-field strength for various compositions.

E_H Hall voltage, V

R Hall coefficient, cc/C

B magnetic-field strength, G

I current, A

t sample thickness, cm

The existence of isothermal conditions was further verified by remeasuring a specimen in high-thermal-conductivity oil (high-grade transformer oil) and obtaining the same Hall coefficient.

RESULTS

The Hall coefficient was found to be negative for all compositions tested, indicating electrons as the predominant carriers. Within the TaC phase region the Hall coefficient became more negative with increasing carbon content (see fig. 4). For stoichiometric TaC a value of about -10×10^{-5} cubic centimeter per coulomb was found, as compared with literature values of -11×10^{-5} cubic centimeter per coulomb (refs. 1, 3, and 4) and -6.4×10^{-5} cubic centimeter per coulomb (ref. 9). The latter value came from poorly characterized materials. The electrical resistivity data of the cubic carbide agreed with those previously reported (ref. 7), decreasing with increasing carbon content (see fig. 4). The magnetoresistivity was too small to be measured accurately, an upper limit of about 10^{-6} being typical under an applied field of 34.4 kilogauss.

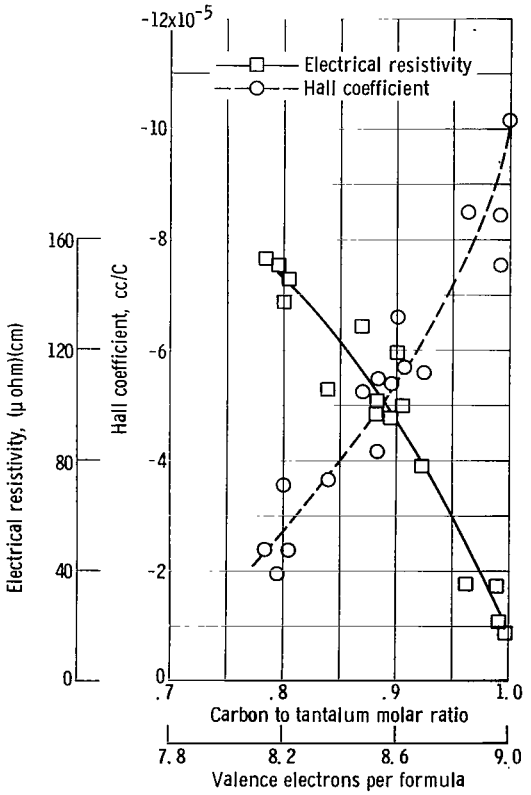


Figure 4. - Room-temperature variation of resistivity and Hall coefficient as functions of carbon content for cubic tantalum carbide.

For the Ta_2C specimen, the Hall coefficient was -15.5×10^{-4} cubic centimeter per coulomb, an order of magnitude more negative than any value derived from the cubic samples. No values have been reported in the literature for this ditantalum carbide. A value of 102 microhm centimeters was found for the electrical resistivity of the Ta_2C sample. Here again

the magnetoresistivity was too small to be measured accurately.

DISCUSSION

It has been assumed that the band structure of the IVth and Vth group transition metal carbides and nitrides are all similar (refs. 10 and 11), and it has been reported that the IVth group carbides exhibit Hall values of an order of magnitude more negative than those for the Vth group (refs. 1 to 4). On the basis of this knowledge and with the previous assumption applied to the present study, the Hall coefficient of TaC would be predicted to become more negative with decreasing carbon content and to approach the value for group IV carbides at a VEC of about 8.0, that is, at $TaC_{0.75}$. The observed variation is opposite to this prediction; as shown in figure 4, the Hall coefficient becomes less negative as carbon content is decreased. The failure of this prediction casts doubt on the validity, even as a first approximation, of applying the band structure of any one of these materials to the entire group by a mere adjustment of the Fermi level in accordance with the VEC.

The findings reported here also show that the one-carrier model cannot be utilized for nonstoichiometric compositions of tantalum carbide, since, based on such a model, the Hall coefficient for the low-carbon samples yields carrier densities which are greater than normal metallic carrier densities. Thus, at $TaC_{0.75}$, the number of conduction electrons would be about 4×10^{23} per cubic centimeter as compared, for example, to about 0.8×10^{23} per cubic centimeter for silver (ref. 12). Furthermore, this electron density for $TaC_{0.75}$ corresponds to about 9 electrons per formula, whereas its VEC is only 8.

The same conclusion can be reached from the following consideration: the variation of the magnetic susceptibility (refs. 13 and 14) and the superconductivity transition temperature (ref. 15) with carbon content in the cubic tantalum carbide phase indicates an increase in the density of states with increased carbon concentration. The electrical conductivity similarly increases. Thus, the number of conduction electrons increases, and this rise, on the basis of a one-carrier model, should be reflected by a decrease in the Hall coefficient, a prediction contrary to the variation in figure 4.

While the one-carrier scheme has been employed to explain the data collected from refractory transition metal carbides and nitrides of stoichiometric composition (refs. 1 and 3) and from their solid solutions (refs. 2 and 3), it is clear that such a scheme is not adequate for nonstoichiometric compositions of cubic tantalum carbide. However, before a unique electrical transport model can be assigned to this system, the factors involved in the conduction process must be ascertained. It is believed that the carbon vacancies greatly influence the conductivity in nonstoichiometric tantalum carbide. It

is important, therefore, to separate this contribution to the conductivity, by means of low-temperature measurements, and to determine its dependence upon composition.

CONCLUSIONS

The room-temperature electrical transport properties of nonstoichiometric tantalum carbides are dominated by negative carriers throughout the entire cubic phase region. A one-carrier model is not adequate to explain the data, and low-temperature measurements are required before a specific model can be proposed.

Lewis Research Center,
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Cleveland, Ohio, September 29, 1965.

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