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(MAGNETIC SUSCEPTIBILITIES OF COMPOSITIONS IN TANTALUM — TANTALUM CARBIDE SYSTEM/

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MAGNETIC SUSCEPTIBILITIES OF COMPOSITIONS IN TANTALUM - TANTALUM CARBIDE SYSTEM*

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SUMMARY

In the tantalum - tantalum carbide (Ta-TaC) system magnetic susceptibility measurements were performed on powder samples, and lattice parameter determinations were conducted on powder and filament specimens. A maximum diamagnetism was observed at $TaC_{0.8}$. The entire Ta_2C phase proved to be paramagnetic, and evidence indicated the zeta phase to be diamagnetic. The dissolution of carbon in tantalum reduced its paramagnetism. The minimum in the susceptibility at $TaC_{0.8}$ could be accounted for by applying the bonding concepts of either Bilz or Dempsey, although their approaches are basically different.

Lattice parameters were determined on the powder samples throughout the entire tantalum - tantalum carbide system and on the filament samples in the TaC phase. The variation in the lattice parameter was nonlinear in the high-carbon end of the face-centered-cubic phase region. The X-ray data from the carbide filament specimens agreed with those from the powder specimens and with the previously reported data from filaments.

INTRODUCTION

An increasing amount of interest concerning the electronic nature of refractory inorganic compounds is evident by the number of papers published on the subject in the last few years (refs. 1 to 10). A better understanding of the electronic nature of these materials may suggest means of utilizing their desirable properties, such as high melting point and corrosion resistance, and of minimizing their brittleness. An important property related to the electronic nature of a material is the magnetic susceptibility.

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*The information presented herein is extracted from a thesis entitled "A Study in the Tantalum-Carbon System" submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physical Chemistry at Western Reserve University, 1964.

In a recently published paper (ref. 11) the author reported the magnetic susceptibility of tantalum carbide (TaC) filaments of various carbon contents in the face-centered-cubic phase region. The extrapolated susceptibility found for the stoichiometric carbide disagreed with that in the literature (ref. 2). This incongruity prompted the present study, in which measurements were performed on powder carbide samples and on an additional carbide filament. In addition, magnetic measurements were made for compositions ranging from the Ta to the TaC phase, including all one- and two-phase regions of the phase diagram. Susceptibility values, as well as the effect of the zeta phase on susceptibilities, are thus reported for the first time for Ta_2C.

X-ray diffraction techniques were used to determine the completeness of the reaction in the preparation of the powder samples, and from these data lattice parameters were determined. Since the previously reported lattice parameters on tantalum carbide filaments given in reference 11 differed from those in the literature (refs. 12 and 13), additional filaments were prepared and X-rayed, and the results were compared with those from the powder carbides.

EXPERIMENTAL PROCEDURE

Material Preparation

High-purity tantalum hydride and spectrographic-grade carbon powders were placed in a carbon crucible and reacted in an induction furnace, some at 1800° C for $1\frac{1}{2}$ hours and others at 2500° C for 10 minutes. The base vacuum was 1×10^{-6} torr. In all cases the outer layer of the reacted material was discarded and the remainder ground and reheated. This process was repeated until no further change in the X-ray pattern could be observed; usually two or three such operations were sufficient. Compositions between tantalum (Ta) and tantalum carbide (TaC) were prepared in this manner.

Several powder preparations of composition $TaC_{0.64}$ and others of $TaC_{0.67}$ were annealed at 1800° C for 20 to 30 hours in an attempt to isolate the zeta carbide, which was first reported by Lesser and Brauer (ref. 13). Carbide filaments in the face-centered-cubic phase region ($TaC_{0.7}$ to $TaC_{1.0}$) were prepared by carburizing tantalum wires in a hydrocarbon gas. Details of this procedure are reported in reference 11.

Chemical and X-Ray Diffraction Analyses

All the products were chemically analyzed for total carbon content. About half were analyzed for free carbon, and several random preparations were analyzed for hydrogen, nitrogen, and oxygen. The free-carbon content from sample to sample amounted to a maximum of 49 parts per million. The hydrogen, nitrogen, and oxygen impurities amounted to maximums of 17, 50, and 190 parts per million, respectively. Repeated analyses on the same sample for total-carbon content gave a precision of $TaC_{x\pm0.01}$. Since the free-carbon content was below the precision of the total-carbon analysis, all compositions for the powders reported herein are for total carbon. The carbide filaments were analyzed only for total carbon.

The X-ray diffraction patterns were made with a 114.6-millimeter-diameter Debye-Scherrer camera by use of copper Kα radiation. For both the carbide filaments and the powder specimens with compositions in the face-centered-cubic phase region, the lattice parameters were calculated by means of a least-squares extrapolation on an IBM 7090 computor. High angle reflections were used for calculating the parameters of specimens with lower carbon content. These data are tabulated in table I.

Magnetic Measurements

The Gouy method was used in determining the magnetic susceptibilities of the filaments. A description of the apparatus is presented in reference 11. The same technique was used on the powder specimens with the following modifications: A 2-millimeter-inside-diameter borosilicate-glass tube, 16 inches long with a glass partition bisecting the tube length, was vertically suspended from a substitutional-weight microbalance in such a way that the partition was centered between the pole caps of an electromagnet. The force developed on the empty tube was only 70 micrograms in a magnetic field of 26.4 kilogauss. A fiducial mark was etched around the upper chamber of the tube 7 inches from the partition. The tube was filled to this mark with sample (-200 mesh) by the addition of small portions at a time, while the tube was continuously tapped to ensure uniform packing within any one sample. French and Harrison (ref. 14) showed that the method of packing (and therefore the tightness of packing) is not a factor in the calculation of the susceptibility so long as the packing is uniform over the length of the sample. The air enclosed in the packed solid, however, is a factor for accurate measurements on materials of small susceptibility. These ideas concerning the packing were verified in the investigation reported herein by repeated determinations of the susceptibility on the same sample filled to the same height in the tube, but varying in its tightness of packing. The resultant gram susceptibilities were within the experimentally determined precision of the measurements, that is, $\pm0.002\times10^{-6}$ electromagnetic unit.

The final equation for the gram susceptibility with the correction for the enclosed air is

TABLE I. - LATTICE PARAMETERS AND PHASES

Carbon-tantalum molar ratio, C/Ta	Type of sample	Reaction temperature, ^{o}C	Phases present (listed in decreasing amount)	Lattice parameter		Standard deviation, A,
				a, A	c, A	
0.99	Powder	2500	TaC only	4.4547	-----	0.0005
.99	Powder	2500		4.4557	-----	.0005
.97	Powder	2500		4.4545	-----	.0004
.96	Powder	2500		4.4557	-----	.0005
.95	Powder	2500		4.4543	-----	.0005
.95	Filament	2000		4.4540	-----	.0009
.95	Filament	2000		4.4536	-----	.0007
.93	Powder	2500		4.4548	-----	.0004
.93	Powder	2500		4.4516	-----	.0005
.92	Filament[a]	2000		4.4526	-----	.0009
.92	Filament	2000		4.4512	-----	.0014
.92	Powder	2500		4.4498	-----	.0004
.92	Filament[a]	2000		4.4490	-----	.0010
.91	Filament	2000		4.4492	----	.0012
.91	Powder	2500		4.4507	-----	.0007
.88	Filament	2000		4.4435	-----	.0004
.88	Filament[a]	2000		4.4430	-----	.0007
.85	Powder	2500		4.4419	-----	.0004
.83	Powder	2500		4.4383	-----	.0005
.82	Powder	2500		4.4387	-----	.0007
.82	Powder	2500		4.4366	-----	.0006
.81	Filament[a]	2000		4.4326	-----	.0014
.81	Filament	2000		4.4316	-----	.0010
.81	Filament	2000		4.4287	-----	.0010
.80	Filament	2000		4.4275	-----	.0016
.79	Powder	2500		4.4291	-----	.0004
.79	Filament[a]	2000		4.4280	-----	.0009
.75	Powder	2500		4.4254	-----	.0006
.75	Filament[a]	2000		4.4251	-----	.0012
.72	Filament	2000	TaC	4.4162	-----	.0009
			Ta_2C (few weak lines)	------	-----	------
.71	Filament	2000	TaC	4.4134	-----	.0004
			Ta_2C (few weak lines)	------	-----	------
.69	Powder	1800	TaC	4.418	-----	------
			Ta_2C (weak lines)	3.104	4.939	------
			Zeta (weak lines)	------	-----	------
0.65	Powder	1800	TaC	4.416	-----	------
			Ta_2C	3.105	4.937	------
			Zeta (weak lines)	-----	-----	------
.64	Powder[b]	1800	TaC	4.416	-----	------
			Zeta	-----	-----	------
			Ta_2C	3.105	4.937	------
.62	Powder	2500	TaC	4.418	-----	------
			Ta_2C	3.103	4.936	------
.60	Powder	2500	TaC	4.414	-----	------
			Ta_2C	3.103	4.936	------
.59	Powder	1800	TaC	4.416	-----	------
			Ta_2C	3.105	4.939	------
			Zeta (weak lines)	-----	-----	------
.56	Powder	1800	TaC	4.415	-----	------
			Ta_2C	3.106	4.937	------
			Zeta (weak lines)	-----	-----	------
.54	Powder	2500	Ta_2C	3.105	4.938	------
			TaC	4.412	-----	------
.53	Powder	2500	Ta_2C	3.106	4.939	------
			TaC	4.413	-----	------
.47	Powder	2500	Ta_2C only	3.106	4.938	------
.46	Powder	1800	Ta_2C only	3.106	4.939	------
.44	Powder	1800	Ta_2C	3.103	4.937	------
			Ta (weak lines)	3.299	-----	------
.41	Powder	1800	Ta_2C	3.106	4.939	------
			Ta	3.306	-----	------
.37	Powder	1800	Ta	3.306	-----	------
			Ta_2C	3.102	4.939	------
.24	Powder	1800	Ta	3.306	-----	------
			Ta_2C	3.101	4.940	------
.02	Powder	1800	Ta only	3.306	-----	------

[a] Data from ref. 11.

[b] Annealed 30 hr after reacting.

$$\chi = \frac{2g(\Delta W - \Delta W_c)}{H^2 - H_0^2} \frac{h}{W} + \frac{k_a}{d}$$

where

χ	gram magnetic susceptibility, emu
g	gravitational constant, g-cm/sec^2
ΔW	apparent change in weight due to magnetic field on sample and tube, g
ΔW_c	apparent change in weight of empty tube, g
H	magnetic field strength at center of pole caps, gauss
H_0	field strength at top of sample, gauss
h	height of sample, cm
W	weight of sample, g
k_a	volume susceptibility of air, emu
d	true density of material, g/cm^3

The X-ray density was used for d in the equation. This substitution assumes that the individual sample particles were free of pores. Any error introduced by this assumption is probably within the precision limits of the method. The magnetic field was measured directly with a rotating-coil gauss meter.

RESULTS

The magnetic susceptibility variation in the Ta-TaC region is shown in figure 1. The phase boundaries in this diagram were determined from data obtained by X-ray diffraction and metallographic techniques and from data in reference 15. The salient features found in this magnetic investigation are as follows: Carbon decreases the susceptibility of tantalum, the entire compositional range of the Ta_2C phase is paramagnetic, a minimum susceptibility χ occurs in the TaC phase at about $TaC_{0.8}$($\chi = -0.121\times10^{-6}$), and $TaC_{1.0}$ is paramagnetic ($\chi = 0.054\times10^{-6}$). Although direct measurements throughout the entire Ta_2C phase are lacking, the values from the terminal compositions of this phase suggest that increasing carbon content lowers the susceptibility.

As shown in figure 1, the region between Ta_2C and TaC was investigated with three different groups of samples. Powders that were reacted at 2500° C showed no evidence of the zeta phase in X-ray diffraction patterns, and the susceptibility data for this material defined a linear variation in this two-phase region. The X-ray patterns from powders reacted at 1800° C for $1\frac{1}{2}$ hours contained some weak zeta lines. The susceptibility plot for these samples, however, produced the same straight line between Ta_2C and TaC as did the samples containing no zeta phase. Any effect the small amount of the zeta phase present had on the susceptibility was thus less than the precision of the measurements. A powder sample of composition $TaC_{0.64}$ reacted at 1800° C and annealed at 1800° C for 30 hours showed a rather well-developed zeta X-ray pattern, in addition to Ta_2C and TaC lines. The susceptibility of this sample was more strongly diamagnetic than samples containing no zeta phase or very small amounts of zeta phase. While the zeta phase was not isolated, it can thus be inferred to be a diamagnetic material. By a comparison of X-ray diffraction intensities, about one-third of this sample was estimated to be the zeta phase. With the use of this estimate and the assumption of a law of mixtures, the gram susceptibility of the zeta phase was calculated to be approximately -0.2×10^{-6} electromagnetic unit.

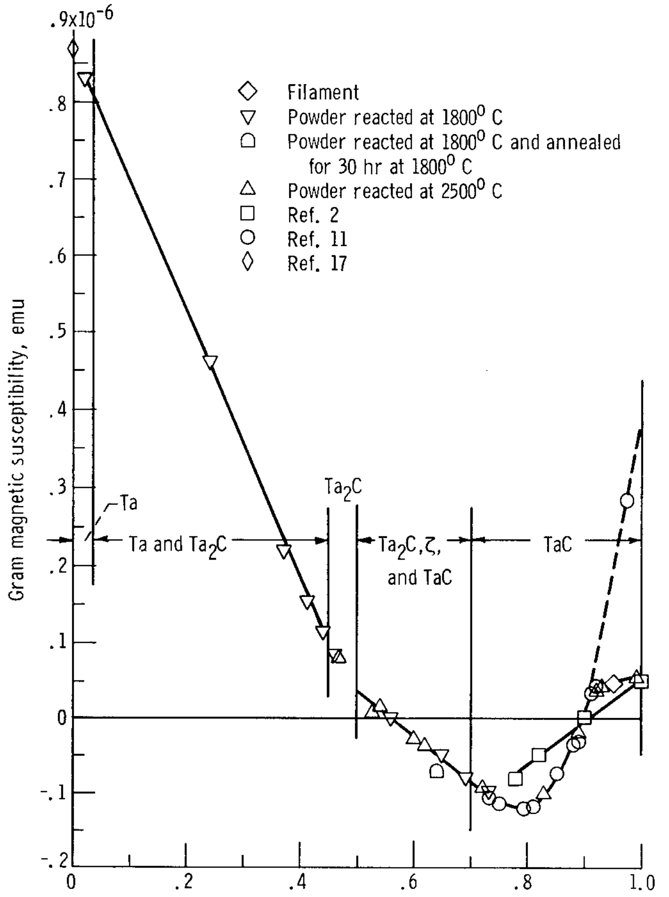

Figure 1. - Variation of magnetic susceptibility of tantalum - tantalum carbide system with composition.

The susceptibility variation in the TaC region as previously determined with filament specimens (ref. 11) was confirmed by the results on the powder samples and the additional filament, except for compositions with a higher carbon content than $TaC_{0.92}$. The high values previously reported for the high-carbon region of the curve were due to an extrapolation through only one point not in agreement with the results presented herein (see dashed line in fig. 1). Based on the numerous points in this region obtained from this investigation and their agreement with the literature, the present results for the high-carbon region of the curve are considered correct.

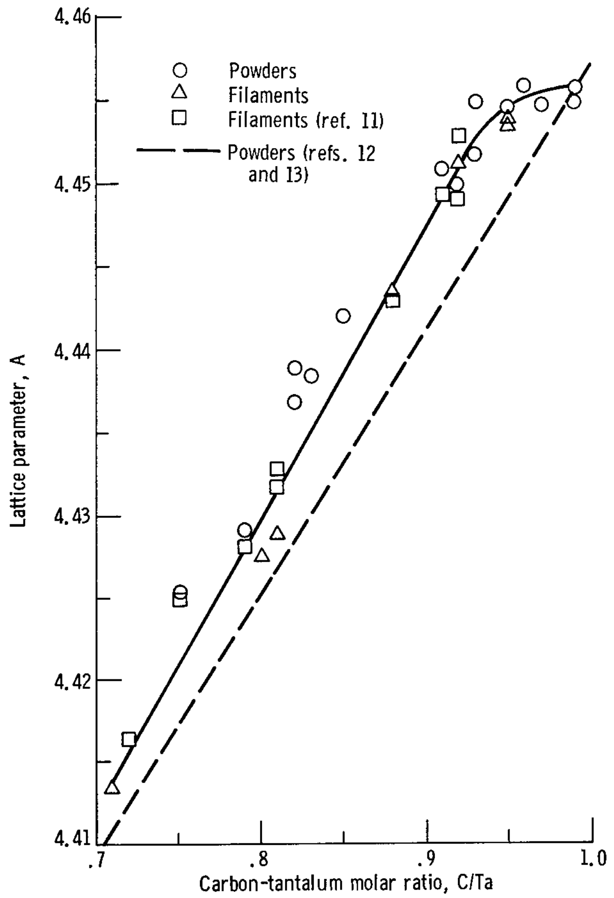

Figure 2. - Variation of lattice parameter with composition in tantalum carbide phase region.

The lattice parameters within the TaC region for both the filaments and powders are presented in figure 2 as a function of carbon content. These data together with the X-ray results outside the TaC region are listed in table I for completeness. Included in figure 2 are the data previously reported on carbide filaments (ref. 11) and the curve of Bowman (ref. 12), whose results agree with those of Lesser and Brauer (ref. 13). The data in references 12 and 13 were obtained from powder samples. Except for the stoichiometric composition, where there is agreement, the results from the two types of specimens prepared in this investigation differ from those of references 12 and 13. The values reported herein are consistent with each other and with the previously reported data of reference 11, but the lattice parameters are larger than those reported in references 12 and 13, and the curve is nonlinear at the high-carbon end. The lattice parameter of the stoichiometric composition was also verified by values obtained for TaC from compositions in the two-phase region, TaC and C.

The discrepancy between the variation found in this investigation and in the literature is puzzling, particularly in view of the fact that the powder samples used in the three investigations were prepared by similar methods and possessed comparable purity. If the variation of the lattice parameter with carbon content in the TaC phase were linear, however, it would be the only member of that group of carbides with the NaCl-type crystal structure formed from a Group IV A or V A transition metal that would behave in this way. The curves for these other systems tend to level off near the high-carbon end with some even displaying a maximum (ref. 15). The lattice parameters outside the TaC region (table I) agree with the literature (ref. 15) within the accuracy of the determinations.

DISCUSSION

According to the theoretical calculations of Bilz (ref. 16), a minimum in the density-of-states curve for face-centered-cubic carbides and nitrides of the Group IV A and V A transition metals should occur at an energy level corresponding to a valence electron concentration per formula[1] of between 8 and 9 (see fig. 3). Reference 16 further mentions the possibility that this minimum in the density of states could produce a minimum in the magnetic susceptibility since the lower-lying p-bands are filled at about 8 valence electrons, and any additional electrons would strongly increase the Fermi limit to higher-lying d-bands accompanied by increased paramagnetism due to the unfilled d-shell. These conclusions are consistent with the minimum in susceptibility found in this investigation at $TaC_{0.8}$, as this composition contains 8.2 valence electrons per formula. Also according to reference 16 the minimum in the density-of-states curve is associated with maximum bond strength. The bonding increases as the p-bands are being occupied and then rapidly decreases as additional electrons begin to fill the weaker bonding states in the higher-lying d-bands. This scheme is in agreement with the previously reported maximum in microhardness at $TaC_{0.8}$ (ref. 11).

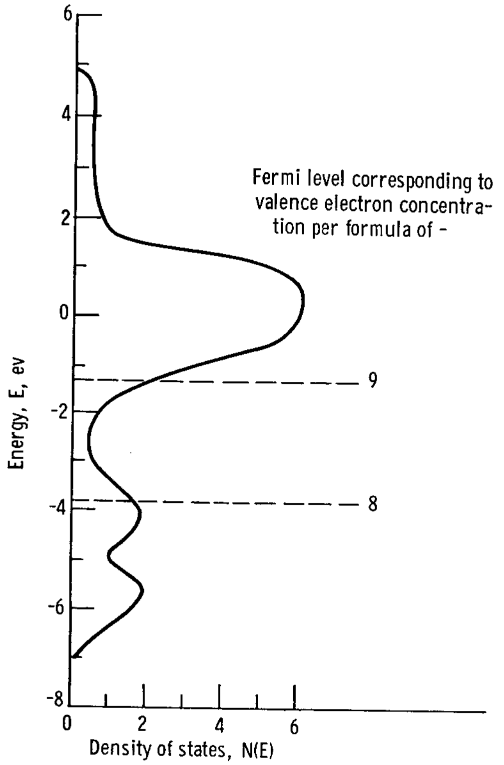

Figure 3. - Density-of-states curve (from ref. 16).

Dempsey (ref. 8), however, offers another explanation for the bonding in these materials that can be used to account for the minimum susceptibility in TaC. From a consideration of melting points on a large number of compounds it is assumed that the nonmetal contributes all its p-electrons to the d-band formed by the metal atoms in compounds like TaC. The d-band of the compound is believed to consist of two subbands; the filling of one of these subbands to about 6 electrons leads to greater stability (bonding strength), and the filling of the other subband reduces the stability. The number of electrons in the d-band of stoichiometric TaC is 6.5 per metal atom (ref. 8): 4.5 contributed by the metal atom (0.5 being in the s-band) and 2 electrons contributed by the p-shell of the carbon atom. For $TaC_{0.8}$, the number of electrons in the d-band

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[1] The valence electron concentration for TaC, for example, is 5 + 4 = 9, and for $TaC_{0.8}$ it is 5 + (0.8)(4) = 8.2.

would thus be about 6.1, enough to fill the bonding subband completely. This situation represents the optimum for maximum bonding strength. It should also result in a minimum in the magnetic susceptibility since all the electron spins would be paired in a filled band.

Although both concepts can account for the minimum in the susceptibility at $TaC_{0.8}$, they differ from each other in a very fundamental way. Whereas the formation of important directional bonds between the metal and the nonmetal atoms with superimposed nondirectional bonds is proposed in reference 16, the band structure of the compound is considered in reference 8 to be essentially of the type normally associated with pure transition metals but with additional electrons in the d-band contributed by the nonmetal. That two basically different concepts can be used emphasizes the need for continued experimental studies. Further, the composition $TaC_{0.8}$ is not the only one of interest in this phase region. The slope of the magnetic susceptibility curve levels off at about $TaC_{0.93}$, the same composition at which the upper trend in the lattice parameter variation begins to level off. Also at this composition the decreasing trend in the room-temperature electrical-resistivity curve (ref. 11) begins to level off.

CONCLUSIONS

This study of the magnetic susceptibility of the tantalum - tantalum carbide (Ta-TaC) system revealed a maximum diamagnetism at $TaC_{0.8}$ and a lowering in the slope of the curve at $TaC_{0.93}$. The entire Ta_2C phase proved to be paramagnetic, evidence indicated the zeta phase to be diamagnetic, and dissolved carbon reduced the paramagnetism of tantalum. It was shown that the minimum in the susceptibility at $TaC_{0.8}$ could be explained by applying the bonding concepts of either Bilz or Dempsey, although their approaches are basically different.

Lattice parameters on powder samples were determined throughout the entire Ta-TaC system and on filament specimens in the TaC region. The variation in the lattice parameter was nonlinear in the high-carbon end of the face-centered-cubic phase region, contrary to the findings of Bowman and of Lesser and Brauer. The X-ray data from carbide filament specimens agreed with those from powder specimens and with the previously reported data from filaments. Throughout the remainder of the system, the experimental lattice parameters agreed with those reported in the literature.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 12, 1964.

REFERENCES

1. Bittner, H., and Goretzki, H.: Magnetic Measurements in the Systems: TiC-ZrC, TiC-HfC, ZrC-HfC, TiC-VC, TiC-NbC, TiC-TaC and NbC-TaC. Monatsh. Chem., vol. 91, 1960, pp. 616-619.

2. Bittner, H., and Goretzki, H.: Magnetic Researches on the Carbides TiC, ZrC, HfC, VC, NbC and TaC. Monatsh. Chem., vol. 93, 1962, pp. 1000-1004.

3. Bittner, H., et al.: Concerning Some Monocarbide-Mononitride Systems and Their Magnetic Properties. Monatsh. Chem., vol. 94, 1963, pp. 518-526.

4. Tsuchida, Takashi, et al.: Hall Effect in the Carbides of Transition Metals. Jour. Phys. Soc. Japan, vol. 16, no. 12, Dec. 1961, pp. 2453-2456.

5. Giorgi, A. L., et al.: Effect of Composition on the Superconductivity Transition Temperature of Tantalum Carbide and Niobium Carbide. Phys. Rev., vol. 125, no. 3, Feb. 1, 1962, pp. 837-838.

6. Cooper, Jeanette R., and Hansler, Richard L.: Variation of Electrical Resistivity of Cubic Tantalum Carbide with Composition. Jour. Chem. Phys., vol. 39, no. 1, July 1963, pp. 248-250.

7. Ingold, J. H.: Thermionic Properties of Some Refractory Metal Carbides. Jour. Appl. Phys., vol. 34, no. 7, July 1963, pp. 2033-2039.

8. Dempsey, E.: Bonding in Refractory Hard Metals. Phil. Mag., ser. 8, vol. 8, 1963, pp. 285-299.

9. Piper, J.: Galvanomagnetic Measurements. Research on Physical and Chemical Principles Affecting High-Temperature Materials for Rocket Nozzles. Quarterly Prog. Rep., Jan. 1-Mar. 31, 1962, Union Carbide Res. Inst., Mar. 1962.

10. Piper, J.: Galvanomagnetic Measurements. Research on Physical and Chemical Principles Affecting High-Temperature Materials for Rocket Nozzles. Quarterly Prog. Rep., Jan. 1-Mar. 31, 1963, Union Carbide Res. Inst., Mar. 1963.

11. Santoro, Gilbert: Variation of Some Properties of Tantalum Carbide with Carbon Content. Trans. AIME, vol. 227, Dec. 1963, pp. 1361-1368.

12. Bowman, Allen L.: The Variation of Lattice Parameter with Carbon Content of Tantalum Carbide. Jour. Phys. Chem., vol. 65, no. 9, Sept. 1961, pp. 1596-1598.

13. Lesser, Richard, and Brauer, Georg: Carbide Phases in Tantalum. Zs. f. Metallkunde, vol. 49, Dec. 1958, pp. 622-625.

14. French, C.M., and Harrison, D.: The Accuracy of Determination of the Magnetic Susceptibility of Solids by the Gouy Method. Jour. Chem. Soc., 1953, pp. 2538-2540.

15. Storms, Edmund K.: A Critical Review of Refractories. Pt. I. Selected Properties of Group IVa, Va, and VIa Carbides. Rep. LAMS-2674, Los Alamos Sci. Lab., Feb. 1, 1962.

16. Bilz, Heinz: Electronic States of Hard Materials with Sodium Chloride Structure. Zs. Physik, vol. 153, 1958, pp. 338-358.

17. Schmidt, F.F.: Tantalum and Tantalum Alloys. Rep. DMIC-133, Battelle Memorial Inst., July 25, 1960.

NASA-Langley, 1965 E-2679

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