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Some Observations Concerning the Maximum in the Lattice Parameter vs Composition Curve of the Group 4a Carbides⁽¹⁾

by

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(1) This work was done under the auspices of the Atomic Energy Commission.

Abstract

Recent reports of a maximum in the lattice parameter vs composition curves of TiC and ZrC have been supported by this study. There is also an indication that this behavior is shared by HfC as well. A comparison between the x-ray and pycnometer density places an upper limit to the metal-vacancy concentration at 5 ± 3 per 1000 metal atoms. In view of this small concentration, it is concluded that the maximum is not due to the presence of such vacancies in the lattice.

Introduction

The observations reported recently of a maximum in the lattice parameter vs composition curves of TiC⁽²⁾ and ZrC⁽³⁾ are sufficiently novel to warrant

(2) J. T. Norton and R. K. Lewis, N63-18389 (1963), Work supported by the National Aeronautics and Space Administration, Contract NASr-98.

(3) R. V. Sara, C. E. Lowell and R. T. Dolloff, WADD-TR-60-143 (1963) Part IV, Work supported by Aeronautical Systems Division, Air Force Systems Command, U.S.A.F.

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some confirmation and an explanation. Many of the compounds formed between the transition elements and B, C, N, and O have a constant crystal structure over a wide range of composition. As the stoichiometry of these phases is reduced, the lattice parameter is usually found to decrease but, in a few cases, has been found to increase. A decrease is generally attributed to the collapse of the lattice into the vacant lattice sites produced by the removal of nonmetal atoms. An expansion under the same conditions is assumed to be due to the filling of metal atom vacancies by additional metal atoms. It is therefore necessary to examine the carbide systems with greater precision than has been employed in the past to determine if metal atom vacancies exist in sufficient concentrations to cause an anomalous effect in their lattice parameter. This was done by comparing the x-ray and pycnometric densities.

Experimental

The powdered carbides and dried xylene were mixed in a glass pycnometer to make the density measurements. Distilled water was used to determine the volume of the pycnometer and the density of the xylene. All weights were corrected to vacuum. During an eight month period, three measurements gave values which were within 0.1% for the xylene density and within 0.03% for the pycnometer volume. Complete saturation of the powder was insured by evacuating the pycnometer after it had been partially filled with liquid. In addition, after the pycnometer had been completely filled and capped, it was again placed under reduced pressure and any tendency for

the fluid to rise in the side tube was noted. If this occurred, most of the xylene was removed and the evacuation-agitation procedure was repeated.

In spite of this care, intragranular voids would still remain unfilled.

Because these carbides are very brittle and were reduced from an arc-melted button in a diamond mortar, one would expect the pieces to fracture through the small number of voids. The difference between the x-ray and pycnometer measurements leads to a maximum possible error of about 0.5%. In the case of HfC, because of the Zr correction, the error could be somewhat higher. Measurements on several other carbides which show no lattice parameter maximum were made to further evaluate the accuracy of the technique.

Lattice parameters were obtained from powder diffraction patterns using Cu radiation ($\lambda_{\alpha_1} = 1.54051$, $\lambda_{\alpha_2} = 1.54433$) and a 114.6 mm Debye-Scherrer camera. A Nelson and Riley extrapolation and its least-squares standard deviation were obtained using an IBM-7090.

The TiC, ZrC and HfC samples were reduced to a -100 mesh powder from arc-melted buttons in a helium dry-box. The other carbides were prepared by heating the powdered elements together, in vacuum, and were screened to -325 mesh. All preparations were done under conditions which experience has shown to result in pure materials.

Discussion

Recent lattice parameter measurements of TiC are compared in Fig. 1, including the data obtained in this study. Except for the composition of $\text{Ti}\bar{\text{C}}$,⁽⁴⁾ the agreement is excellent. This work indicates that $\text{Ti}\bar{\text{C}}$, after

⁽⁴⁾As has been proposed by W. Worrell, a bar will be used when a phase boundary composition is meant, thereby eliminating the need to state what the composition might be.

being quenched from the melt, has a composition very near $\text{TiC}_{1.0}$. The two phase samples studied by Norton and Lewis,⁽²⁾ although they might represent the composition at a lower temperature, probably were not at equilibrium. This is suggested because they contained only a small amount of carbon and were heated for only a short time (2-3 hr at 1950°). It should be noted that even after being arc-melted and being held at 1800° for 14 hr, a sample of $\text{TiC}_{0.904}$ (Table 1) still contained 970 ppm unreacted free carbon. In this study, $\text{TiC} + \text{C}$ was held in a molten state for a total of at least 5 min., while the eutectic temperature was being measured by a thermal analysis technique.⁽⁵⁾

⁽⁵⁾E. K. Storms, LA-2942 (1964)

The lattice parameters of ZrC are compared in Fig. 2. Except for the composition of one point reported by Farr,⁽⁵⁾ the data agree very well. In both figures, earlier work has been ignored because it was based on material having an uncertain oxygen content. This study also supports earlier observations that $\text{Zr}\bar{\text{C}}$, after being quenched from the melt, has a composition of about $\text{ZrC}_{0.95}$.⁽⁵⁾

The very poor agreement between the various lattice parameter values reported for HfC can be improved somewhat if they are corrected for the zirconium content. A variable oxygen content probably accounts for the remaining scatter. The material used in this study contained 1.27% ZrC, and the values listed in Table 1 have been corrected by assuming that Vegard's Law holds between ZrC and HfC of the same composition. Although this work is hardly conclusive, it does suggest a lattice parameter maximum in this system.

The presence of metal atom vacancies was investigated by comparing the pycnometric and x-ray densities. Unfortunately, the major errors in density measurements lead to a low value. Therefore, the resulting metal vacancy concentration must be viewed as an upper limit. These results are tabulated in Table 1. The column marked "x" refers to the subscript in the formula $M_x C_y$ and its value was calculated by the equation

$$x = a_o^3 D_{\text{pyc.}} / 6.6412 (M + \frac{c}{m} C)$$

where

$D_{\text{pyc.}}$ = pycnometric density

a_o = lattice parameter in angstrom units

M = atomic weight of the metal

C = atomic weight of carbon

$\frac{c}{m}$ = mole ratio.

It would appear from the measurements that an upper limit to the vacancy concentration is 5 ± 3 per 1000 metal atoms. Neutron diffraction studies of

TiC also have indicated that the metal-vacancy concentration is low. ⁽⁶⁾

⁽⁶⁾ N. S. Gorbunov, N. A. Shishakov, C. G. Saidkov and A. A. Babad-Zakhryapin, Izv. Akad. Nauk S.S.S.R., otd. Khim., Nauk 1961, 2093-5

If the lattice parameter maximum is indeed due to metal vacancies, they must exert a surprising influence. However, in view of this essentially negative result other explanations must be sought.

⁽⁷⁾ I. Cadoff, J.P. Nielsen and E. Miller, Plansee Proc. 1955, 50.

⁽⁸⁾ C.P. Kempter and R.J. Fries, Analytical Chem. 32, 570 (1960).

TABLE 1

Composition c/m	Pycnometric Density, at 25.2°C g/cm ³	Lattice Parameter, Å	X-ray Density, g/cm ³	X	(%M+%C)	Remarks
TiC _{0.904}	4.815	4.3306 ± 0.0003	4.805	1.002	99.93	corrected for 970 ppm free carbon
TiC _{0.988}	4.854	4.3275 ± 0.0004	4.898	0.991	100.00	corrected for 2.47% free carbon
ZrC _{0.855}	6.457	4.7009 ± 0.0001	6.488	0.995	99.44	corrected for 0.2% free carbon
ZrC _{0.970}	$\left\{ \begin{array}{l} 6.593 \\ 6.582 \end{array} \right.$	4.6988 ± 0.0002	$\left\{ \begin{array}{l} 6.586 \\ 6.586 \end{array} \right.$	$\left\{ \begin{array}{l} 1.001 \\ 0.999 \end{array} \right.$	100.08	corrected for 530 ppm free carbon
HfC _{0.985}	12.595	4.6400 ± 0.0001	12.645	0.996	99.6	corrected for 1.27% ZrC _{0.975} and 700 ppm free carbon
HfC _{0.993}	12.556	4.6389 ± 0.0001	12.669	0.991	100.35	corrected for 1.27% ZrC _{0.99} and 0.11% free carbon, contains 500-700 ppm oxygen
NbC _{0.825}	7.731	4.4562 ± 0.0001	7.717	1.002	99.92	
NbC _{0.924}	7.708	4.4665 ± 0.0002	7.752	0.994	99.84	
NbC _{0.980}	7.729	4.4701 ± 0.0003	7.783	0.993	99.2	corrected for 0.68% free carbon
TaC _{0.99}	14.423	4.4555 ± 0.0002	14.480	0.996	99.48	corrected for 0.27% free carbon