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Estimation of thermal expansion behaviour of some refractory carbides and nitrides

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Lattice parameters of some refractory carbides and nitrides were estimated up to 2400 K using an empirical approach. The computed lattice parameters are in very close agreement (±0.5%) with the values calculated from experimental thermal expansion data reported in the literature. This empirical approach with modifications may be applicable to the prediction of the thermal expansion behaviour of other classes of high temperature materials.

1. Introduction

In recent years, there has been an increasing demand for high performance materials for use in high temperature and aerospace applications. Refractory borides, carbides, nitrides, and oxides have been actively considered for these purposes. These compounds are also being investigated for use in high-temperature composites as reinforcements, matrices, and coatings. However, many thermophysical and chemical data for these refractory materials are not available with reasonable accuracy. One of these is the thermal expansion coefficient at high temperatures. In composites, the nature and properties of fibre/matrix interfaces are affected by the mismatch between the thermal expansion of the fibre and matrix. During the fabrication of composites and their use at high temperatures, stresses are generated around the fibres and at the interfaces owing to thermal expansion mismatch. Accurate data on the thermal expansion of these materials are also required for the selection and development of coating materials. A good thermal expansion match is necessary for the coating's adherence to the substrate and for its resistance to thermal stresses. In addition, thermal expansion data are also very useful in the joining of materials.

In the literature [1] thermal expansion data are available for only very few refractory materials in the high temperature range with a reasonable degree of accuracy. The reported experimental data have uncertainties of about ± 5% at lower temperatures and about ± 10% or more at higher temperatures. Thus, a computation of accurate thermal expansion coefficients by theoretical or empirical methods is highly desirable for the selection of candidate materials for high-temperature applications. In addition, due to experimental problems associated with high-temperature measurements, theoretically estimated data can be used in the selection of candidate materials for a given application.

2. Background and rationale

At present, there are only a few methods available for the prediction of the thermal expansion behaviour of high temperature materials. Touloukian *et al.* [1], Zharkov and Kalinin [2], and Kittel [3] have applied theoretical approaches using a quasi-harmonic approximation such as the Debye equation of state which requires input values of heat capacities, Grüneisen parameters, and isothermal bulk moduli or equivalent data in terms of other parameters. These parameters are not readily available for ceramic materials, which seriously limits the above theoretical approaches. Keppler [4] and Krikorian [5] described empirical methods that have been useful for predicting the thermal expansion coefficients of metals and ionic compounds. These correlations are based on the melting points. Krikorian [5] reported that for pure metals with a b.c.c., f.c.c. or h.c.p. structure, there is a volume expansion of about 8% between absolute zero and the melting point, whereas for alkali halides the corresponding value is about 14%. In the case of high-temperature materials like MgO and Al_2O_3, these values are 14% and 5%, respectively [1]. The empirical formulations presented by the above authors [1–5] cannot be applied to refractory materials due to their poor correlation with the available experimental data. Krikorian [6, 7] estimated the thermal expansivity of refractory compounds using atomization energy and microhardness data within ± 10%. Hazen and Finger [8, 9] used an empirical correlation to determine the average thermal expansion coefficients between room temperature and 1273 K. Because even a small lattice mismatch can cause the failure of components, there is a need for a reliable prediction of the thermal expansion of these materials at high temperatures. In this paper, an equation is presented which allows an estimation of the lattice parameters of refractory carbides and nitrides up to high temperatures very accurately.

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Details of the equation and its application are given below.

3. Results and discussion

The mean coefficient of thermal expansion is the most commonly reported parameter of experimental thermal expansion studies. The refractory metal carbides and nitrides have combinations of covalent and metallic bonding. The interatomic forces are influenced by many factors such as crystal structure, atomic radii, co-ordination number, and the type of bonding. With increasing bond strength between two atoms, the interatomic distance decreases.

Empirically, an equation was developed for the estimation of high temperature lattice parameters which is based on room temperature lattice parameters and relevant structural and bonding parameters. This equation is as follows

$$a_T = a_{298} + S^2 n \frac{r_a + r_c}{z_a + z_c} 10^{-4} \Delta T \qquad (1)$$

where a_T and a_{298} are the lattice parameters at temperature T and 298 K, S^2 is the ionicity factor, n is the co-ordination number, r_a and r_c are CN12 atomic radii of the constituents [10], and z_a and z_c are the anion and cation valence. Values of S^2, defined as ionicity factor and given by Hazen and Finger [8, 9], are 0.20 for all carbides and nitrides. All the refractory carbides and nitrides considered here have the co-ordination number 6. Teatum *et al.* [11] gave radii for elements based on a co-ordination number twelve (CN12) which have been obtained using the observed interatomic distances in the f.c.c. (A1), b.c.c. (A2), and h.c.p. (A3) structures and adjusting these distances for CN12. In addition, Teatum *et al.* [11] have also taken some of the radii from Pauling [12] and converted to angstrom units and to CN12. A detailed description of CN12 and other radii for elements has been given by Pearson [10]. The values of the input data used in the present investigation are given in Table I. Room temperature lattice parameters of all the materials in Table II, are from Eckerlin and Kandler [13].

From the lattice parameters, the per cent linear thermal expansion and linear thermal expansion coefficient (α) are calculated using the following standard relationships

$$\frac{\Delta a}{a_{298}} = \frac{a_T - a_{298}}{a_{298}} \times 100 \qquad (2)$$

TABLE I Structural and chemical data used in the present study

Element	Valency	CN12 radius (nm)
Ti	4	0.1462
Zr	4	0.1602
Hf	4	0.1580
V	5	0.1346
Nb	5	0.1468
Ta	5	0.1467
W	6	0.1408
C	4	0.0916
N	− 3	0.0880

TABLE II Lattice parameters of some refractory carbides and nitrides at 298 K

Compounds	Lattice parameter (nm)
TiC	0.4326
ZrC	0.4691
HfC	0.4640
VC	0.4168
NbC	0.4471
TaC	0.4456
WC	0.4215
TiN	0.4242
ZrN	0.4578

TABLE III Comparison of literature and computed values of lattice parameters (nm) for some refractory carbides and nitrides at different temperatures

Compounds	Temperature (K)				
	500	1000	1400	2000	2400
TiC(*L*)	0.4332	0.4348	0.4363	0.4389	0.4408
(*P*)	0.4333	0.4351	0.4366	0.4387	0.4401
ZrC	0.4696	0.4712	0.4727	0.4752	0.4770
	0.4699	0.4718	0.4733	0.4755	0.4771
HfC	0.4646	0.4662	0.4682[a]	0.4695	0.4709
	0.4648	0.4666	0.4689	0.4704	0.4719
VC	0.4173	0.4187	0.4200	0.4218	0.4225[b]
	0.4174	0.4189	0.4201	0.4219	0.4226
NbC	0.4476	0.4491	0.4505	0.4528	0.4546
	0.4478	0.4493	0.4506	0.4525	0.4538
TaC	0.4461	0.4475	0.4488	0.4509	0.4525
	0.4463	0.4478	0.4491	0.4510	0.4523
WC	0.4219	0.4228	0.4237	0.4251	–
	0.4221	0.4235	0.4246	0.4263	–
TiN	0.4248	0.4268	0.4294[a]	–	–
	0.4251	0.4271	0.4295	–	–
ZrN	0.4584	0.4601	0.4617	0.4644	–
	0.4587	0.4608	0.4626	0.4650	–

L = lattice parameters calculated from per cent linear thermal expansion data from the literature, and *P* = present work ([a]1600 K, [b]2200 K).

TABLE IV Literature and calculated values of per cent linear thermal expansion for some refractory carbides and nitrides at different temperatures

Compounds	Temperature (K)				
	500	1000	1400	2000	2400
TiC(*L*)	0.138	0.513	0.859	1.453	1.902
(*P*)	0.161	0.577	0.924	1.410	1.733
ZrC	0.101	0.446	0.771	1.302	1.678
	0.170	0.576	0.895	1.364	1.705
HfC	0.129	0.466	0.897[a]	1.188	1.482
	0.172	0.560	1.056	1.379	1.702
VC	0.133	0.476	0.768	1.218	1.368[b]
	0.143	0.503	0.792	1.223	1.391
NbC	0.123	0.458	0.762	1.280	1.671
	0.156	0.492	0.782	1.207	1.498
TaC	0.122	0.443	0.727	1.205	1.557
	0.157	0.493	0.785	1.211	1.503
WC	0.084	0.319	0.529	0.856	–
	0.142	0.474	0.735	1.138	–
TiN	0.156	0.613	1.238[a]	–	–
	0.214	0.686	1.251	–	–
ZrN	0.142	0.524	0.872	1.451	–
	0.209	0.675	1.049	1.603	–

L = percentage linear thermal expansion data from literature, and *P* = present work ([a]1600 K, [b]2200 K).

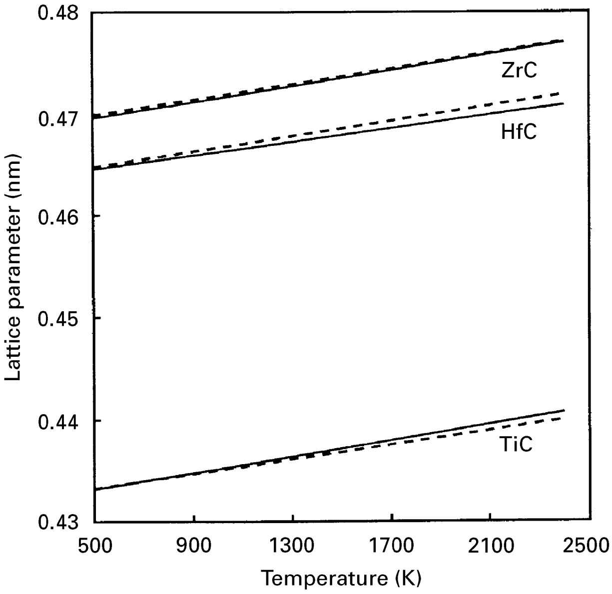

Figure 1 Lattice parameters of TiC, ZrC, and HfC as a function of temperature (solid line literature and dashed line present work).

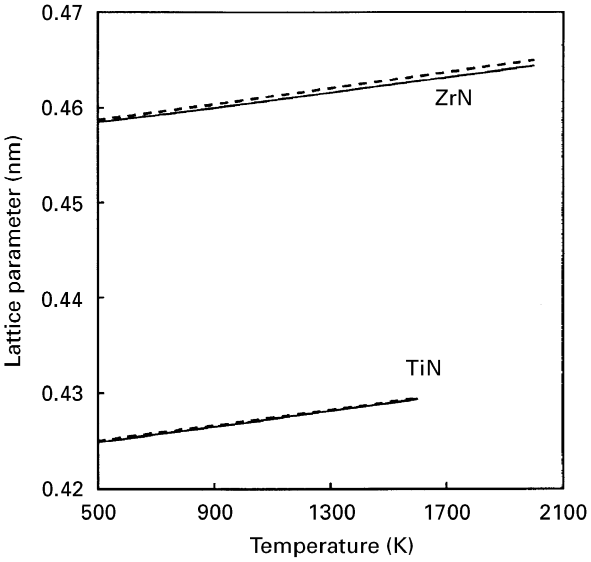

Figure 2 Lattice parameters of TiN and ZrN as a function of temperature (solid line literature and dashed line present work).

and

$$\alpha = \frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\Delta a}{a_{298}}\right) = \frac{1}{a_{298}}\frac{\mathrm{d}a}{\mathrm{d}T} \qquad (3)$$

Lattice parameters of refractory carbides (TiC, ZrC, HfC, VC, NbC, TaC and WC) and nitrides (TiN and ZrN) were calculated using Equation 1. The computed lattice parameters and per cent linear thermal expansion data for some carbides and nitrides are given in Tables III and IV. Literature values [1] for these compounds are also given for comparison. The lattice parameters of some refractory carbides and nitrides as a function of temperature are plotted in Figs 1 and 2. A good correlation (± 0.5%) between literature and computed lattice parameters is observed.

Work is in progress for the application of this approach to other materials and will be reported later.

4. Conclusions

The close agreement between computed lattice parameters of some refractory carbides and nitrides versus temperature and the literature is quite promising for other applications. Although our approach to the prediction of lattice parameters at elevated temperatures is empirical, it is useful for the estimation of the thermal expansion behaviour of the above materials.

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