THERMAL EXPANSION OF TUNGSTEN MONOCARBIDE

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INTRODUCTION

TUNGSTEN Monocarbide (WC) is an interstitial compound and has a simple hexagonal structure.[1-4] Like most other interstitial compounds, it is a technologically important and structurally interesting substance. It combines in its physical behaviour the characteristic metallic property of decreasing electronic conductivity with increasing temperature with typical covalent peculiarities like hardness and brittleness.[5] This strange combination of properties is due to an interplay of non-directional metallic bonds between tungsten atoms and the directed covalent bonds between tungsten and carbon atoms.[6] These features of the WC structure are also likely to be reflected in other physical properties, particularly in the anisotropy of its mechanical behaviour and thermal expansion. Not much work appears to have been done on the directional dependence of the mechanical properties, probably because of the difficulty of obtaining suitable single crystals. There is only one report available showing that WC exhibits anisotropy in its microhardness.[7] Its elastic anisotropy has recently been estimated from measurements on X-ray line broadening and displacement by Ivensen *et al.*[8] The directional thermal expansion has been investigated by Becker[9] and Belikov and Umanskii.[10] Although in both these reports the nature of anisotropy in thermal expansion is similar, there are large differences in the magnitudes of the principal coefficients and also in the amount of the anisotropy (Table II). Further, as discussed later in this paper, the nature of the anisotropy reported by these workers does not appear to be in accord with either the nature of bonding involved in the structure[6] or the elastic anisotropy reported by Ivensen *et al.*[8] Hence a fresh and systematic study of the temperature variation of the lattice parameters of the crystal over a restricted range of temperature, was undertaken by the authors.

EXPERIMENTAL AND RESULTS

X-ray powder pictures of tungsten monocarbide at different temperatures were taken employing a high temperature symmetrical focusing camera[11] and CuK radiation. The reflections measured and used in calculations were $(30\bar{3}0)_{a_1a_2}$, $(30\bar{3}1)_{a_1a_2}$, $(11\bar{2}3)_{a_1}$ and $(21\bar{3}2)_{a_1a_2}$. The lattice parameters were evaluated by using Cohen's[12] method in combination with the error function $\phi \tan \phi$. Standard errors in the values of the parameters were evaluated by the method of Jette and Foote.[13]

Table I gives the values of the lattice parameters along with the estimated errors and the axial ratio at different temperatures. Since both the parameters showed a linear temperature dependence, the data were processed by the usual method of curve fitting and the following expressions were obtained.

TABLE I

Lattice parameters and axial ratio of WC at different temperatures

Temp. °C	a Å	c Å	c/a
25	2·9064 ±·0003	2·8374 ±·0003	0·9762
82	2·9071 ±·0003	2·8377 ±·0003	0·9761
164	2·9083 ±·0004	2·8385 ±·0003	0·9760
218	2·9088 ±·0002	2·8390 ±·0002	0·9760
280	2·9091 ±·0004	2·8396 ±·0003	0·9760

$$a_t = 2{\cdot}90627 + 110{\cdot}13 \times 10^{-7}t$$
$$c_t = 2{\cdot}83709 + 87{\cdot}18 \times 10^{-7}t$$

Here a_t and c_t are expressed in Å and t in °C. The two temperature independent coefficients of expansion were derived from these expressions and are given in Table II, the values from earlier workers being also given for comparison.

TABLE II

Comparison of the thermal expansion coefficients of tungsten monocarbide

Authors	$\alpha_a \times 10^6$/°C.	$\alpha_c \times 10^6$/°C.
Becker[9] ..	5·2	7·3
Belikov & Umanskii[10] ..	3·84	3·90
Present work ..	3·78	3·67

A comparison of the present values of the lattice parameters with those available in literature is also given in Table III.

TABLE III

Comparison of the lattice parameters of WC at room temperature

Author	a Å	c Å	Composition
Metcalfe (1946)[14] ..	2·9063	2·8386	$WC_{1.0}$
Nowotny & Kieffer (1947)[15]	2·9028	2·833	..
Krainer & Konopicky (1947)[16]	2·9066	2·8364	..
Krainer (1950)[17] ..	2·9066	2·8367	..
Leciejewicz (1961)[3] ..	2·9065	2·8363	..
Levinson (1964)[18] ..	2·9084	2·8370	$WC_{0.99}$
Brown *et al.* (1966)[19]	2·9066	2·8374	$WC_{1.007}$
Present work ..	2·9064	2·8374	*$WC_{0.99}$ to $WC_{1.00}$

* Estimated from a comparison of the present lattice parameters with those for well-characterised samples from other sources.[20(a)]

DISCUSSION

The agreement between the present values of the parameters and the others given in Table III, is generally satisfactory, particularly the recent values by Brown *et al.*[19] The data on coefficients of expansion given in Table II show that while the old values given by Becker[9] for both the coefficients are rather high, there is some agreement between the present values and those given by Belikov and Umanskii.[10] However, there is a significant difference worth noting. Belikov and Umanskii report a value of α_c slightly larger than that of α_a, although the difference is not appreciable. The present results differ from this in two respects; firstly the difference between the two coefficients is relatively large and secondly the value of α_c is smaller than that of α_a. Although, it may be argued that much significance cannot be attached to the small differences involved in the above comparison, the plausibility of the present results can be judged from the following reasoning.

The estimates given by Ivensen *et al.*[8] on the elastic anisotropy of WC indicate that the elastic modulus along c-axis is 1·5 times larger than that along a perpendicular direction. This means that in a general way, the binding of the atoms in the crystal is stronger along the c-axis than in the basal plane. Again, as Belikov and Umanskii[10] have pointed out, the fact that the axial ratio is less than unity indicates that the structure is compressed along the hexagonal axis, which obviously is a manifestation of stronger binding along this direction. Further, W-W metallic bond distances in the basal planes are 2·906 Å. As against this, the W-W distances along c-axis are 2·837 Å. These distances are larger than the W-W distances in tungsten metal by 6·3% and 3·8% respectively. As Rundle[6] pointed out, this lengthening is an indication of the weakening of metallic bond by the introduction of carbon atoms in the structure and so it may be said that in WC, the metal-metal bonds are relatively stronger along the hexagonal axis, when compared to those in the basal plane. The bonding between tungsten and carbon atoms in the structure is covalent and these directed bonds make angles of about 50° with the c-axis. Although this would mean that the components of these bond vectors along the c-axis are slightly larger than those in the perpendicular directions, yet these bonds are not very strong as evidenced by the lower melting points of the carbide (2710°–2780° C.), when compared to that of the metal (3410° C.).[20(b)] Therefore effectively the two components could be considered to be not very much different from each other. In other carbides (*e.g.*, TiC, ZrC, HfC and VC, etc.,) where the carbon atoms are octahedrally bonded to metal atoms and the covalent bonds are very strong, the carbides have higher melting points than those of the corresponding metals.[20(b)]

It is worth mentioning here that Belikov and Umanskii who have reported the results on many carbides, calculated the principal coefficients of thermal expansion "from the displacements of the interference maxima for various orientations of the crystallographic planes perpendicular (or nearly perpendicular) to the a and c axes", and it is not clear from their paper, as to which reflections they used in the case of tungsten monocarbide. In view of the above arguments, it is reasonable to conclude that in WC, the thermal expansion along a-axis is more than that along c-axis.

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THE GLOBAL ATMOSPHERIC RESEARCH PROGRAMME (GARP)

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THE International Union for Geodesy and Geophysics created a Committee on Atmospheric Sciences (CAS) and requested it "to develop an expanded programme of atmospheric science research". The CAS was created in June 1964 to advise the International Council of Scientific Unions on matters arising from the following two UN resolutions :

Resolution 1721 (XVI) December 1961, which recommended "members and WMO to study measures to advance the state of atmospheric sciences and technology in order to improve existing weather forecasting capabilities and to further the study of the basic physical processes that effect climate" and Resolution 1802 (XVII) December 1962, which recommended that WMO "develop in greater detail its plan for an expanded programme to strengthen meteorological services and research", and invited ICSU through its unions and national academies "to develop an expanded programme of atmospheric science research which will complement the programmes fostered by the World Meteorological Organization".

Since 1962, a major effort to respond to the two UN resolutions has been made by the WMO resulting in the formulation of the World Weather Watch (WWW) Programme. The last WMO Congress which met in Geneva in April 1967 approved detailed plans for the further developments of the weather observing networks maintained by member nations.

In recent years rather remarkable progress had been made in formulating physico-mathematical models of the atmosphere, treated as a fluid dynamical system, and in using powerful computers to integrate the governing thermohydrodynamic equations to stimulate and forecast the behaviour of the atmosphere. In parallel with this, the development of the meteorological satellite has introduced a dramatic new observational capability. Several countries in middle latitudes now produce objective numerical forecasts of the evolution of weather systems over periods of 2-3 days and these are rapidly superseding traditional methods of forecasting the main features of the pressure, temperature and wind fields, at least in middle latitudes. Using very complex models of the global atmospheric circulation, it has been possible to simulate the major features of the world's climate and to conduct numerical experiments which strongly indicate that it should be possible to produce reliable forecasts of the major features of the weather for about one week ahead.