

Incorporation of Titanium, Tantalum, and Vanadium Into the Hexagonal WC Lattice

A. Pasquazzi*, W.D. Schubert*, E. Halwax*, G. Kremser**

* Vienna University of Technology, Austria

** WOLFRAM Bergbau- und Hütten AG, Austria

Abstract

Based on our earlier work on the formation of a hexagonal (W,Cr)C mixed crystal carbide, the formation of (W,Me)C (Me=Ti, Ta, V, V+Cr) solid solutions was studied in the temperature range of 1450°C to 1950°C. A two step carburization procedure was used for their preparation: In a first step, (W,Me)₂C was formed, which in a second carburization step was then transformed into the (W,Me)C carbide.

Keywords

W-Cr-C, W-V-C, W-Ti-C, W-Ta-C, mixed crystal carbide

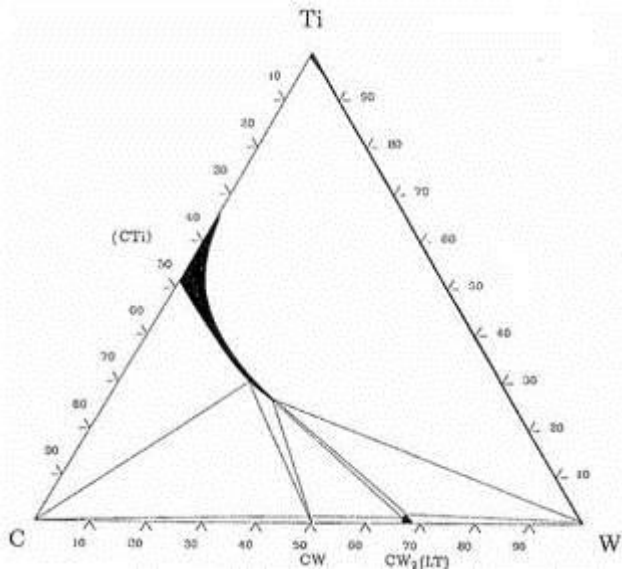
Introduction

WC crystallizes in the non-centrosymmetric space group P-6m2 (No. 187) with one formula unit per unit cell. The cell dimensions are $a = 0.2906$ nm and $c = 0.2837$ nm. Within the group of refractory carbides its solubility for third elements is considered to be generally very low, with the exception of molybdenum, which forms a continuous series of solid solution carbides (W,Mo)C below 1170°C [1]. The solubility of molybdenum in the hexagonal WC was demonstrated to increase with temperature, and at 2600°C only about 26 mol% of "MoC" remains in the solid solution. With increasing amount of Mo the lattice parameters decrease as compared to pure WC, and for the pure MoC the a and c parameters were determined to be 0.29038 and 0.2819 nm, respectively [2].

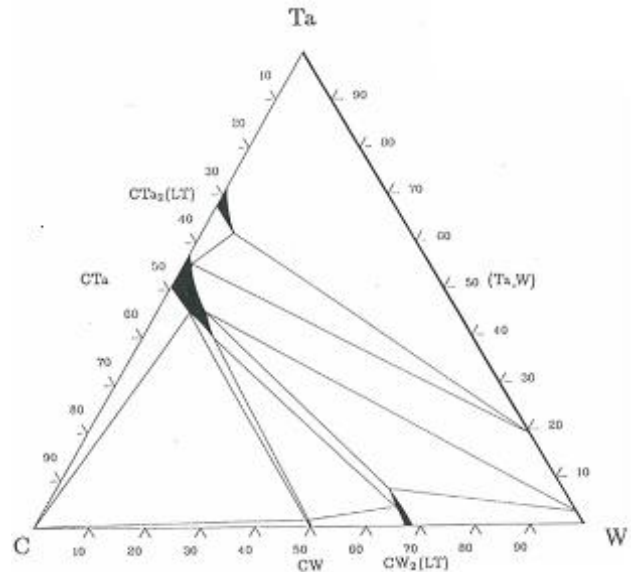
In the case of chromium it was shown that at 1300°C about 8 at% of Cr dissolve into the WC phase at equilibrium with graphite and Cr₃C₂ [3]. More recently, it was then elaborated by Tükör et al. [4] that this amount can be significantly increased to about 15 mol% of "CrC" (5 wt%) through a two-step reaction path. In this case the lattice parameters were shifted towards significantly smaller lattice parameters ($a = 0.2889$ nm and $c = 0.2817$ nm; annealing temperature: T=1200-1450°C).

The strategy of the present work is based on the work of Z. Tükor [4], following the same reaction paths to investigate the solubility of Cr+V, V, Ti and Ta in the hexagonal WC structure. These elements were selected as they show a sufficient solubility in the W_2C -phase (see Fig. 1) [5], which, in previous experiments, turned out to be the main requirement for incorporating higher amounts of the refractory elements into the hexagonal WC structure.

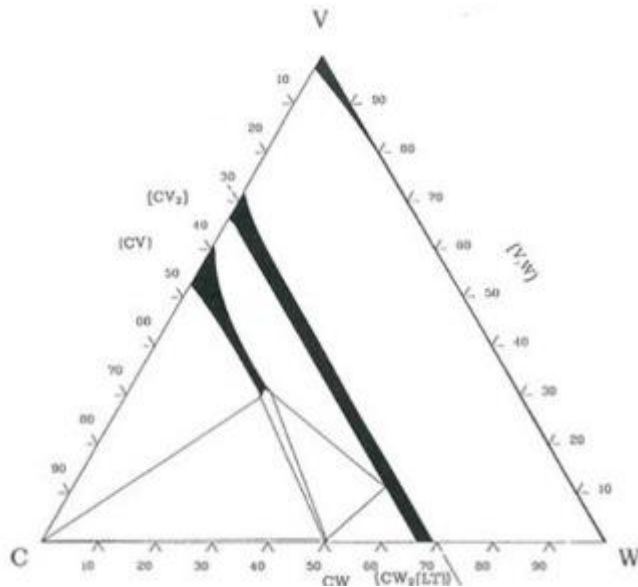
(a) at 1500°C



(b) at 1500°C



(c) at 1500°C



(d) at 1300°C

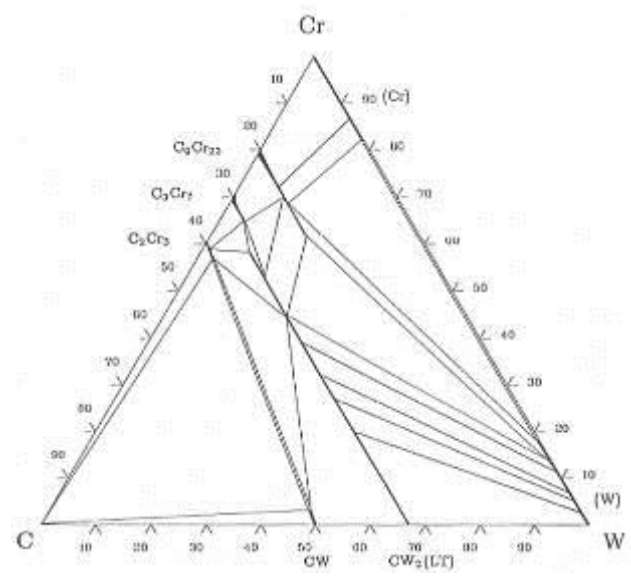


Figure 1: ternary phase diagrams: (a) C-W-Ti; (b) C-W-Ta ; (c) C-V-W ; (d) C-W-Cr-system [5]; reprinted with permission of ASM International. All rights reserved. www.asminternational.org.

Experimental Details

Step 1 (Carburization of Tungsten to W₂C)

First, five different W₂C powders were produced from tungsten powder with a mean particle size of 0.7 μm (FSSS) by carburizing at 1630°C using elemental carbon. The elements V, Ta, Ti, Cr+V were added to the “black mixture” prior to carburization. For reference purposes a W₂C powder without additions was produced. The concentration of the elements in the final W₂C powders were selected to be 3 mol.% V₂C, 3 mol.% Ta₂C, 3 mol.% Ti₂C and 1.5 mol.% Cr₂C + 1.5 mol.% V₂C. Based on Figure 1 all additions should result in the formation of a single phase (W,Me)₂C.

After carburization the subcarbide powders were analyzed by x-ray diffraction. The measurement conditions were: PANalytical X'Pert PRO powder diffractometer, CuK_α radiation (Ni K_β filter), scan range 2θ = 5-90°, X'Celerator detector with a scan length of 2.546°. Silicon was used as an internal standard. Precise lattice parameters were determined from Rietveld refinements using the program TOPAS (ver. 4.1, Bruker AXS, 2008).

Step 2 (Carburization of W₂C to WC)

The final carburization of the W₂C powders was carried out at three temperatures: 1450°C, 1630°C and 1950°C. The produced powders were again analyzed by x-ray diffraction.

Step 3 (Cemented Carbide Production)

The WC powders which were carburized at 1450°C were milled with 10 wt% Co and cemented carbide granules were formed. The granules were pressed at 200 MPa and sintered under vacuum for 1 hour at 1420°C. The resulting cemented carbides were analyzed by scanning electron microscopy. After an HCl (1:1) acid leach of the cobalt binder the resulting carbide powder residue was investigated by x-ray diffraction.

Results and Discussion

Step 1 (Carburization of Tungsten to W₂C)

The XRD data did not show any additional phases attributable to the dope elements. Comparing the lattice parameters *a* and *c* from the differently doped W₂C powders it can be concluded, that elements with a greater atomic radius than tungsten (W: 139 pm; Ti: 147 pm; Ta: 146 pm) tend to enlarge the W₂C lattice and those with a smaller atomic radius than tungsten (V: 134 pm; Cr: 128 pm) tend to downsize the W₂C lattice (Fig. 2). Due to these facts the lattice parameters as derived from the XRD measurements indicate that most of the added elements went dissolved in the W₂C structure.

Step 2 (Carburization of W₂C to WC)

Comparing the lattice parameters *a* and *c* of the fully carburized powders (W,Me)C (Fig 3) it is obvious that at all three carburization temperatures the lattice parameters changed in the case of V, Cr and Ta as compared to the pure tungsten carbide. However, in the case of Ti, the lattice parameters were about the same as those of pure WC. This result indicates that the two step carburization process promotes the

incorporation of V, Cr and Ta into the (W,Me)C phase but not of Ti. Instead a cubic (Ti,W)C_{1-x} phase is formed.

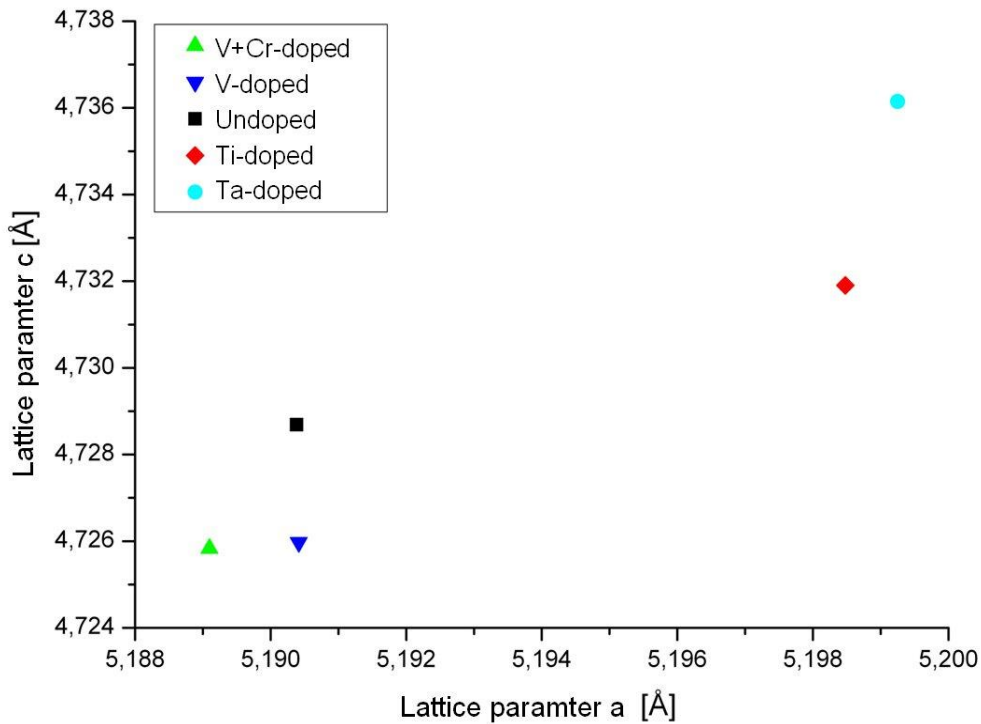


Figure 2: Lattice parameters of the (W, Me)₂C-powders; Me: V, V+Cr, Ti, Ta.

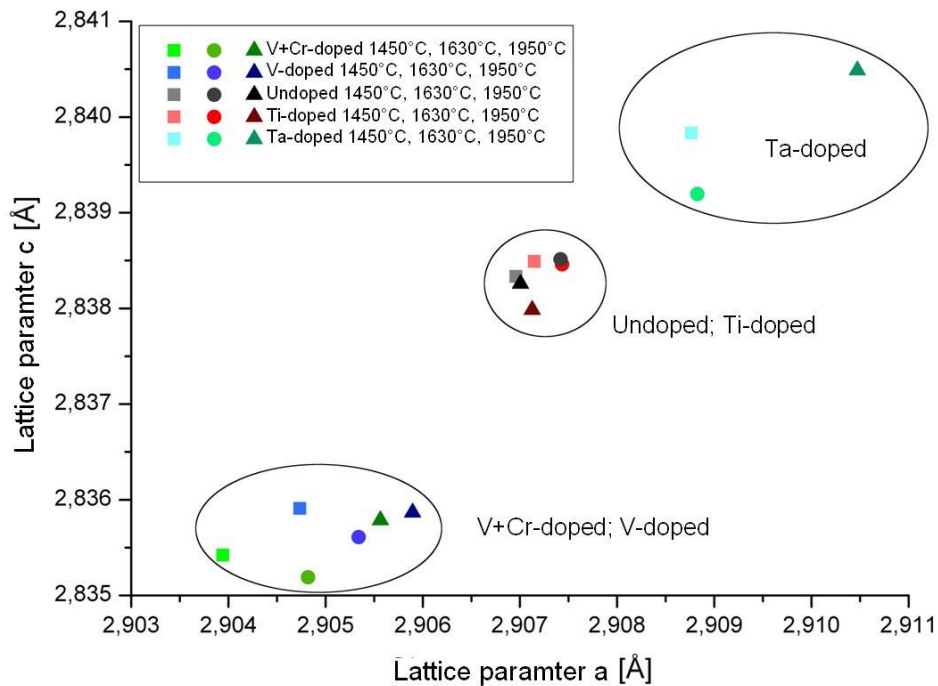


Figure 3: Lattice parameters of the (W,Me)C-powders; Me: V, V+Cr, Ti, Ta; powders carburized at 1450°C, 1630 °C and 1950°C.

It can also be demonstrated that the change in lattice parameters of the (W,Me)C phase correlates with the atomic radii of the dissolved elements (see Fig 4).

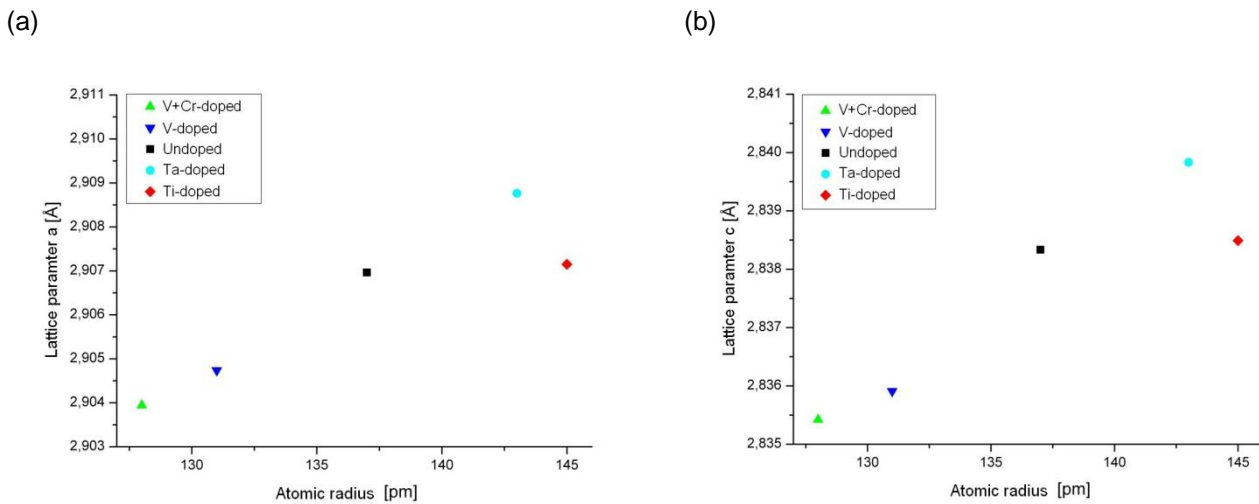


Figure 4 (a, b): Correlation of the lattice parameters *a* and *c* with the atomic radius of the element added. Note that in case of Ti additions (red mark) the parameters remain the same as those of the pure WC (no Ti incorporation!)

Step 3: Cemented Carbides

After sintering, the hardmetals were acid-leached to remove the Co binder. After a soft disintegration of the remaining carbide body the resulting powders were measured by x-ray diffraction (Fig. 5). The XRD data show that for all elements added the lattice parameters of the hexagonal (W,Me)C phases moved towards the lattice parameters of the pure WC after sintering. This is a clear indication that a fraction of the added element has left the structure.

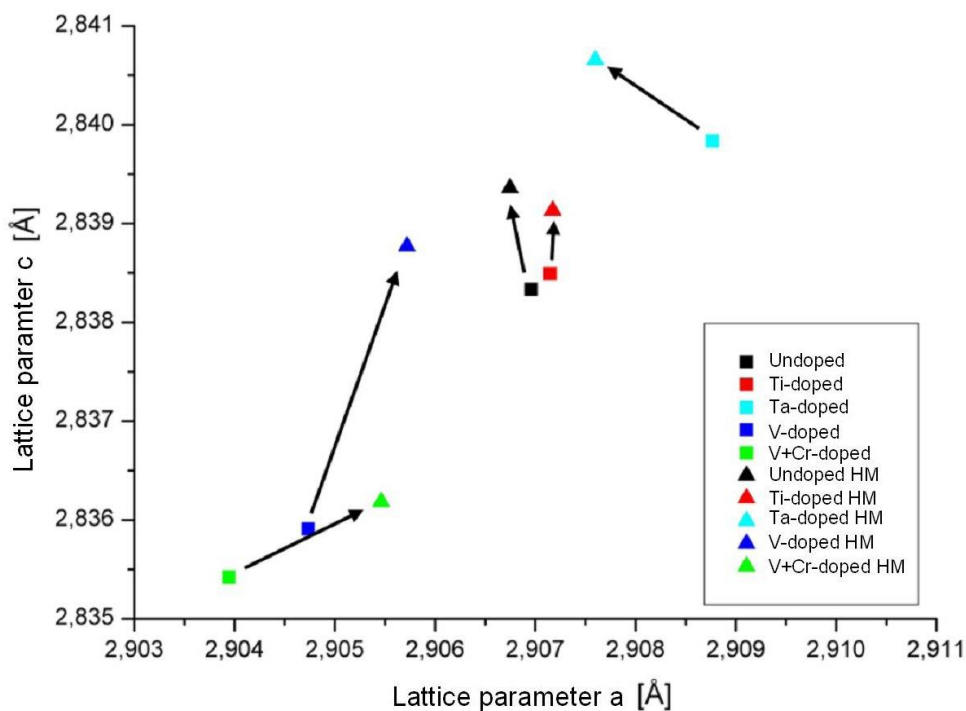


Figure 5: (W,Me)C lattice parameters before and after sintering of cemented carbides; powders obtained after an acid leach.

All those elements that were expelled from the WC structure, with the exception of chromium, therefore, were found as separate cubic carbide phases within the cemented carbide microstructure (see Fig. 6).

The fraction of chromium that had left the structure obviously did dissolve in the cobalt binder, as one would expect from thermodynamic considerations.

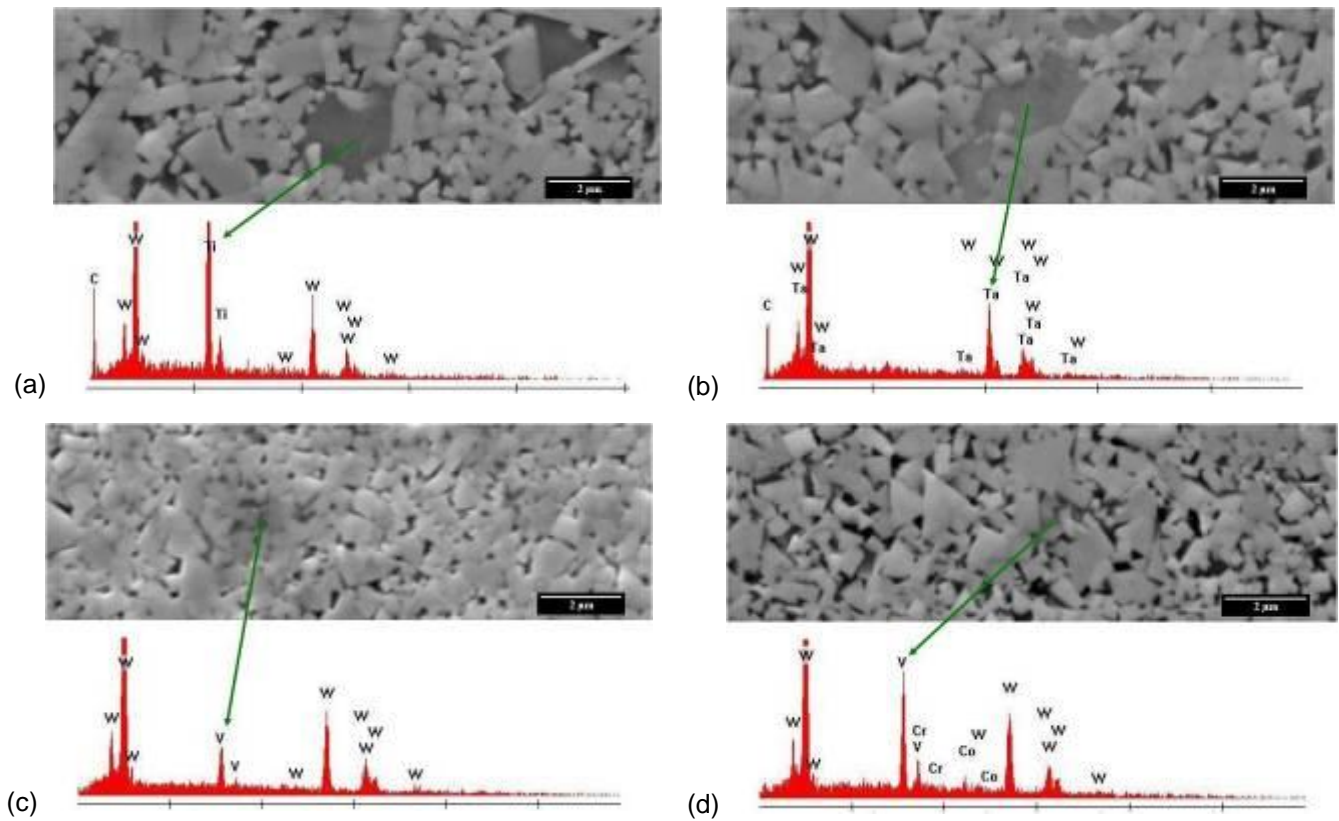


Figure 6: SEM images and EDX spectra of the cubic phases formed during cemented carbide sintering; (a) Ti, (b) Ta, (c, d) V, V+Cr.

Conclusion

The results of our work demonstrate that in addition to Mo and Cr also other refractory elements like V and Ta can be dissolved to a certain extent in the hexagonal WC structure. Ti was dissolved at first in the subcarbide, but was then set free during the transformation into WC. Instead, a cubic $(\text{Ti,W})\text{C}_{1-x}$ was formed.

During sintering of cemented carbides the respective phase equilibria change due to the presence of cobalt, and a certain fraction of the elements which were dissolved at first in the WC $[(\text{W,Me})\text{C}]$ leaves the structure. In the case of Ti, V and Ta, cubic carbides are formed. In the case of Cr, some chromium remains in the carbide and the balance is present in the cemented carbide as a solid solution in cobalt.

References

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