Preparation and properties of \((W,Mo)C\) powders and \((W,Mo)C\)-Co cemented carbides

K. Shi, V. Schwarz, W. Lengauer

Vienna University of Technology, Getreidemarkt 9/164CT, A-1060 Vienna, Austria

Abstract

Hexagonal WC can dissolve a large amount of molybdenum carbide to form a ternary phase \((W,Mo)C\). Thus, it has already been interesting in the past to study the properties of cemented carbides with such a modified hard phase.

\((W,Mo)C\) powder with around 15wt.% “MoC” was prepared by mixing \(WO_3\) and \(MoO_3\) powders, reducing the mixtures under flowing hydrogen at 1000°C. After adding an appropriate amount of carbon black, carburisation was performed at 1600°C. The powder was analysed for carbon (C total: 7.12wt%, C free: 0.24wt%) and grain-size (\(d_{50}: 1.89\mu m\)). The corresponding formula is \(W_{0.76}Mo_{0.24}C\), hence 24% of the W atoms are placed by Mo. Doped \((W,Mo)C\) hardmetals with the same vol% Co as 6, 10 and 12wt%Co in WC-Co hardmetals were then fabricated by vacuum sintering and HIPing. Some typical data such as eutectic temperatures of liquid-phase formation, hardness HV30, Palmqvist-Shetty \(K_C\), density and magnetic properties were recorded.

The liquid-phase formation temperatures of formulations containing eta phase and free C, respectively, are lower than the corresponding temperatures in WC-Co. The fracture toughness is about 10% lower than that of WC-Co hardmetals at the same hardness. This was due to some amount of porosity which did not vanish completely upon HIPing. The grain size was partly very fine, generally, the fine particles are rounded, whereas large particles are prismatic. The latter were frequently found in \((W15Mo)C-12Co\), probably due to too high sintering temperature at a larger Co content. A core-rim type structure is occurring in the prismatic hard-phase particles. Several reasons can account for the inhomogeneous grain-size distribution, such as broad particle size distribution of the starting powder, too high sintering temperature of the Co-rich composition and unequal C activity. The results clearly show that upon optimisation of the starting powder and optimisation of sintering, property levels of WC-Co hardmetals can be reached. Upon such an achievement, the modified microstructure of \((W,Mo)C\)-based hardmetals with spherical grains and presence of Mo could provide some application benefit.

Keywords
cemented carbides, molybdenum carbide, \((W,Mo)C\), powder, sintering, hardness, fracture toughness.
Introduction

By alloying carbides with hexagonal WC, a change of properties of cemented carbides (hardmetals) can be expected. However, only a few carbides, such as that of molybdenum and chromium, are soluble in WC [1-4]. While Cr is known to positively influence the grain-size distribution of WC-Co hardmetals and is well established in hardmetal manufacturing, the use of molybdenum is less frequent [5,6]. This is probably due to the fact that the grain-size-modifying effect of Mo is much smaller as that of Cr or V. Together with Cr, Mo additions on the order of 0.5-1wt% of the hardmetal were claimed to positively influence the hardness/toughness ratio of hardmetals [5]. Recent studies on TiC-containing hardmetals with Mo additions of 1.2wt% have claimed some benefit, too [7,8] which is certainly due to the better wetting of TiC by the binder such as known from cermets [9]. Also for WC-Fe-Ni a positive influence on the TRS and grain size was found at 0.25wt% Mo addition [10].

As the solubility of Mo in the binder phase of WC-Co hardmetals is around 4wt% [11], the above-mentioned doping levels are appropriate for modifying the binder phase composition as well as the WC grain size and the amount of Mo incorporated into the WC grains is probably very small. The problem of attaining a higher Mo concentration is complicated by the fact that there is no stable monocarbide (above 1120°C) and thus no MoC powder is available. Hence, a substantial amount of carbon black must be added together with Mo2C to the starting formulation at higher Mo contents for balancing the C level to avoid eta phase formation. Alternatively, a high C activity of the sintering atmosphere could compensate for some C deficiency, too [6]. The maximum feasible Mo2C addition in the hardmetals was found to be around 1.0 [6] – 5.0wt.% [12]. At higher amounts a substantial fraction of porosity was detected. This is probably due to unbalanced diffusion upon homogenisation of the hard phase occurring upon liquid-phase sintering.

At higher Mo additions than the solubility of Mo in the binder phase, the amount of (W,Mo)C phase increases. (W,Mo)C-based hardmetals were studied already several decades ago [13-19] to study the influence of hard-phase modification, achieve some W substitution and/or introducing nitrogen into the hard phase, because the (W,Mo)C phase can incorporate N, depending on the Mo content. Properties of hardmetals with very high Mo concentrations in the (W,Mo)C phase were the subjected of these studies and the properties of hardmetals were rather poor and did not justify any application. This is certainly partly due to the substantial reduction of hardness upon increasing the Mo concentrations of 25mol% on the metal sublattice [20] together with restricted powder quality and sintering technology at that time.

Recently, we have performed a study by means of state-of-art laboratory techniques that the Mo content in (W,Mo)C could be increased to 15wt% “MoC” without much deterioration of the hardmetal properties [12]. Due to the lack of (W,Mo)C powder this was performed by hot-pressing WC+Mo2C+C in order to form a homogeneous (W,Mo)C hard phase. The hot-pressed samples were then crushed and milled for preparation of hardmetals. In the present study, the hard phase powder was prepared by mixing and reducing oxides with a following carburisation.
Experimental

Commercially available powders were used from Treibacher Industrie AG (WO₃, VC and Cr₂C₃), H.C.Starck (carbon black Luvocarb), Umicore (Co Ultrafine) and purchased from Sigma-Aldrich (MoO₃).

**Powder and hardmetal preparation**

(W,Mo)C powder with 15wt% MoC was obtained by reduction and carburisation of mixed oxides MoO₃ and WO₃. For that purpose, oxide powders of appropriate weight ratio were mixed in a drum mill in cyclohexane for 48 h, using hardmetal balls with a diameter of 6mm as grinding media. The weight ratio of grinding media to powder was 10:1. After milling, the oxide slurries were placed in a vacuum oven and dried at 70°C for 6h. The powders were then filled in a Mo container in an Al₂O₃ boat, and reduced in a tube furnace under flowing high-purity hydrogen at 1000°C for 5h. Subsequently, the reduced powder was mixed with carbon black, filled into a graphite crucible and carburised at a maximum temperature of 1600°C. The carburised powder was then milled in an attritor (NETZSCH PE075) with hardmetal lining and hardmetal stirrer for 4h upon 400r/min in cyclohexane under Ar atmosphere. The ball to powder weight ratio was 10:1 and the flow rate of Ar was 0.1L/min.

(W,Mo)C-Co-VC-Cr₂C₃ samples with three different Co contents, 6.67, 11.04 and 13.24wt%, were fabricated using the attritor-milled powders. The content in vol% of Co is the same as that of WC-Co hardmetals with 6, 10 and 12wt%Co, respectively. For simplification, we will refer in the following to the content of WC-Co hardmetals. The compositions of investigated specimens are given in Table 1. W15Mo from the reduction step of the oxides or carbon black were added to adjust the carbon content of the samples. The powder blends were mixed in the same drum with the same parameters as mentioned above. Afterwards, the mixtures were separated from milling balls with a set of sieves and then dried at 70°C. For the carbon adjustment mixing was done using a tubular mixer for 3h. The green bodies were pressed at 30kN to form cylinders of size 12.8mm in diameter and 6mm in height. All the specimens were sintered in a vacuum furnace in a graphite crucible with a maximum sintering temperature of 1440°C for 60min (dwell time) first in vacuum and above 1100°C under an Ar pressure of 100mbar. Afterwards, the samples were HIPed at 1440°C for 30min at a pressure of the 50bar Ar.

Table I: Composition of investigated specimens. The alloys have the same vol% Co content as WC-6wt%Co, WC-10wt%Co and WC-12%Co, respectively.

<table>
<thead>
<tr>
<th>Hardmetal type</th>
<th>(W15Mo)C wt%</th>
<th>Co wt%</th>
<th>VC wt%</th>
<th>Cr₂C₃ wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(W15Mo)C-6Co</td>
<td>92.91</td>
<td>6.67</td>
<td>0.12</td>
<td>0.30</td>
</tr>
<tr>
<td>W15MoC-10Co</td>
<td>88.26</td>
<td>11.04</td>
<td>0.20</td>
<td>0.50</td>
</tr>
<tr>
<td>(W15Mo)C-12Co</td>
<td>85.92</td>
<td>13.24</td>
<td>0.24</td>
<td>0.60</td>
</tr>
</tbody>
</table>
Characterisation of powders

Carbon analysis was performed by carrier-gas hot extraction (CGHE) with a Leco SC 200 analyser. For analysing the free carbon, the powder was decomposed in HNO₃/HF, the undissolved C separated by filtering and measured by CGHE. Particle-size distribution was made by laser diffraction with a CILAS 1064 analyser whereas the powder was dispersed in water (with dispersion aid) by use of ultrasound. For phase identification X-ray diffractometry (XRD) with Cu-Kα radiation was utilized.

Differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA)

DTA/TG was performed with a Linseis STA 1700 DSC-DTA/TG equipped with a MoSi₂ heater. Typically, 200mg of powder was pressed to pellets of 5mm diameter and inserted into an alumina crucible. Heating was usually performed employing two zig-zag temperature profiles to observe the phase reaction in the green body (1st heating) as well as in the sintered body (2nd heating). High-purity Ar atmosphere was used. The weight change was recorded in the first heating cycle. All heating/cooling rates were +/- 10°C/min. The temperature readings were corrected by melting pure metals as well as by means of the Co-C eutectic at 1320°C.

Characterisation of sintered samples

The samples were cut, ground and diamond polished down to 1µm and etched with fresh Murakami solution (3s etching time) to detect eta phase and free C by light-optical microscopy LOM (Olympus GX51). Scanning electron microscopy (SEM) in BSE mode was utilized to observe the microstructure of polished non-etched surfaces.

The density of the sintered samples was measured by the Archimedes method according to EN ISO 3369:2010 standard. Characterisation of magnetic properties including magnetic saturation (MS) and coercive force of the samples were measured using a Koerzimat (CS 1.096 Foerster, Germany). The MS values were related to pure Co (with Cr taken into account) to receive the specific saturation magnetisation in % of pure Co. An EmcoTest M4U-025 hardness tester was used to measure the hardness (HV30) and calculate the Palmqvist-Shetty fracture toughness (KIC) according to DIN ISO 3878 using 5 indentations.

Results and discussion

Analysis and phase composition of (W15Mo)C powders

The total carbon content of XRD-single-phase (W15Mo)C powder was 7.12wt% with a free C content of 0.25wt%. Thus, the hard phase seems to be stoichiometric with respect to the C/metal ratio. Fig.1(a,b) shows the XRD results of (W15Mo)C powders carburised at 1400 and 1600°C, respectively. It is obvious that the powder carburised at 1400°C for 90min contains (W,Mo)₂C subcarbide (Fig.1(a)), whereas upon heating at 1600°C for 60min complete carburisation and single-phase (W,Mo)C was obtained (Fig.1(b)). Although the free C content of the powder carburised at 1600°C is relatively high it is not visible in the pattern.
Figure 1: XRD patterns of the (W15Mo)C powders carburised at 1400 (a) for 90min and 1600°C (b) for 60min. At the lower temperature the carburisation was not complete.

Fig.2(a) shows a SEM image of the powder carburised at 1600°C after attritor milling. A rather uniform grain size can be assumed from this image. Upon embedding the powder into resin and polishing, no inhomogeneities were detected inside the particles judged from the grey scale in the BSE image in Fig.2(b).

Figure 2: SEM-BSE images of (W15Mo)C powder after attritor milling for 4h (a) powder bed, (b) embedded and polished powder.

The particle-size distribution (Fig.3) shows that the powder has a relatively broad particle-size distribution, probably due to agglomerates which cannot be broken in the ultrasonic treatment. From this analysis, the particle size $d_{50} = 1.89\mu m$ and the average grain size is $2.25\mu m$. 
Figure 3: Grain-size distribution (histogram) and accumulated grain size (red line) of the single phase (W15Mo)C powder carburised at 1600°C after attritor milling for 4h; $d_{50} = 1.89\mu m$, average = 2.25\mu m.

**Liquid-phase formation / weight change**

Fig.4 shows the differential thermal analysis (DTA) results of the 2nd heating of the (W15Mo)C-Co samples with eta and free C, respectively. A data evaluation gives 1292°C onset and 1316°C for the peak maximum for the equilibrium with eta phase, and 1232°C onset and 1266°C for the peak maximum for the equilibrium with free C. These temperatures are substantially lower than the corresponding invariant reactions in the WC-Co system (as indicated). In addition, they are dependent on the C content because the reactions are no more invariant (four components).

![DTA curves](image)

Figure 4: DTA curves (2nd heating) of (W15Mo)C-30Co with free carbon (blue) and eta phase (red).

Fig.5 shows the TGA curves of the (W15Mo)C-Co samples with eta and free C, respectively. It is obvious that there are three stages in both, the (W15Mo)C-Co-eta and (W15Mo)C-Co-free C samples. These steps are due to the CO formation upon release of oxygen by the various phases involved under the
action of C. The second step has the largest weight loss compared to that of the other two steps. The first step is due to the CO release due to binder phase reduction, the second and third due to W-rich and Mo-rich hard phase, respectively. This means that a full homogeneity in the prepared powder was not achieved, contrary to results shown in Fig.2(b).

![TGA curves of (W15Mo)C-Co with eta and free-C.](image)

**Microstructures of (W15Mo)C-Co hard metals**

Fig.6 shows the LOM images of the (W15Mo)C alloys with 6, 10 and 12%Co, respectively, with different carbon content adjusted by addition of W15Mo or carbon black. With increasing of carbon content (from top to bottom), the phase composition changes from (W15Mo)C-Co+eta over two-phase alloys to (W15Mo)C-Co+C. Even in the two-phase samples, porosity was detected although a HIP treatment was employed. This phenomenon remains unclear yet, some inhomogeneity of the employed powder with some diffusion reactions occurring upon could be an explanation. Support for such an assumption comes from the fact that a too high Mo:C addition causes porosity, too [6,12].

Figs.7(a)-(c) show the SEM images of (W15Mo)C-Co hard metals in the two-phase region after sintering and HIP treatment at 1440°C. The grain size is not uniform. Relatively large carbide grains with sharp edges and corners were detected mainly in (W15Mo)C-12Co and partially in (W15Mo)-6Co, whereas in (W15Mo)C-10Co much more finer spherical grains are seen. The observation is consistent with the particle-size distribution shown in Figs.8(a)-(c), which indicate that (W15Mo)C-12Co has the largest grain size with grains of up to 3-3.5µm. This is because the (W15Mo)C-12Co samples have the highest binder phase content, which promotes the grain growth during sintering and HIP treatment, possibly at a too high sintering and HIPing temperature, too. The inhomogeneous grain size could also be triggered by the presence of W15Mo necessary for adjusting the C level. A peculiar distribution of W and Mo in the hard-phase grains occurs upon sintering, as can be observed from the grey scale (darker: more Mo, lighter more W). Some grains with a core-rim structure exist, with a with white-grey (W rich) or dark-grey (Mo rich) cores. Sometimes this core-rim structure is threefold, which a white core, an inner dark-grey rim and a medium-grey outer rim, which was described in an earlier study, too [12].
Figure 6: LOM images of (W15Mo)C-Co alloys with different carbon content. Addition from top to bottom row: 1.5% W15Mo, 1.0% W15Mo, 0.5wt% W15Mo, no addition, 0.2wt% C. 2: two-phase sample (no eta phase or free C), +C: free carbon, eta: eta phase present.
Figure 7: SEM images of (W15Mo)C-Co alloys, (a) (W15Mo)C-6Co (b) (W15Mo)C-10Co (c) (W15Mo)C-12Co. The arrows in Fig.7(c) indicate grains with core-rim structure, white arrows indicate grains with white-grey core and the black arrows indicate grains with dark-grey core.

Figure 8: Grain-size distribution by linear intercept evaluation of two-phase samples of (W15Mo)C-Co alloys, (a) (W15Mo)C-6Co, (b): (W15Mo)C-10Co, (c): (W15Mo)C-12Co. Note the larger grain-size range in (c).
Properties of 15MoWC-Co hardmetals

Fig. 9 shows the density of the (W15Mo)C hardmetals with the three different Co contents (compare to Fig. 6) upon addition of W15Mo or C. Using lattice parameters of [3], the X-ray density was calculated for (W15Mo)C to 14.05 g/cm³ and hence the three hardmetal grades have 13.71, 13.48 and 13.37 g/cm³, respectively. These values are far from the measurements and the difference between theoretical and measured density does not account for the porosity alone (the maximum porosity is on the order of A06B02 for two-phase alloys shown in Fig. 6). It is clear that the calculation of the theoretical densities cannot take the solubility into account, hence, the true amount of phases with their true densities is unknown.

Figure 9: Density of (W15Mo)C-Co alloys with different carbon content, compare to Fig. 6. 2: two-phase, η: additional eta phase, C: additional free carbon.

Fig. 10 shows the magnetic saturation of the three hardmetal grades (shown in Fig. 6). Interestingly, almost same MS values show different phases present and the MS is not always higher, the higher C content (indicated by the presence of phases). This behaviour is not clear yet, it could be due to sample inhomogeneities and that the MS of such hardmetals does not behave like that of WC-Co.

Figure 10: Magnetic saturation of (W15Mo)C-Co hardmetals with different carbon content, compare to Fig. 6. 2: two-phase, η: additional eta phase, C: additional free carbon.
Coercive force ($H_c$) data are presented in Fig.11 and are highest for the 10%Co grade (except for 1.5wt%W addition) and lowest for the 12%Co grade. In WC-Co hardmetals the $H_c$ values reflect the grain size of WC (the higher $H_c$ the finer the grain size). This corresponds also to the SEM microstructures in Fig.7 with the impression that the 10%Co grade has the finest grain size and also to the data given in Fig.8.

![Graph showing coercive force vs. W15Mo or C addition](image)

Figure 11: Coercive force of (W15Mo)C-Co hardmetals with different carbon content, compare to Fig.6. 2: two-phase, η: additional eta phase, C: additional free carbon.

The reason for the somehow scattered data of magnetic saturation (Fig.10) and coercive force (Fig.11) as a function of the W15Mo or C addition could also be due to the fact that the high solubility of W and Mo in the binder phase [11] is different due to differences in C activity.

The hardness (HV30) and fracture toughness ($K_{IC}$) data of the (W15Mo)C-Co two-phase hardmetals (Fig.6) are shown in Fig.12 and compared to that of WC-10Co hardmetals. The results show that all the (W15Mo)C-Co samples have lower toughness at the same hardness than WC-Co hardmetals. However, if it is taken into account that many decades of development have been necessary for WC-Co hardmetals, the achieved fracture toughness is not far from the target and it can be assumed that upon optimisation of the (W,Mo)C-type hardmetals the level of WC-Co hardmetals can be reached.

![Graph showing hardness vs. Vickers hardness HV30](image)

Figure 12: HV30 and $K_C$ of two-phase (W15Mo)C-Co alloys (see microstructures in Figs.6, 7 and other data in Figs.8-11).
Conclusions

Preparation of (W15Mo)C powder has been investigated from reduced oxide mixtures, which were then carburised at temperatures up to 1600°C. A series of (W15Mo)C-Co based hardmetals with different cobalt contents have been prepared. The powders and hardmetals were characterised by various methods.

DTA investigations show that the liquidus temperatures of alloy with free C and eta phase, respectively, are substantially lower than that of the corresponding WC-Co hardmetals. The carburised powder was uniform in composition according to SEM but contained a substantial amount of free C which made doping by W15Mo necessary. This doping was in a range which probably influences the grain-size distribution negatively – with occurrence of large grains. Some porosity which was present even after HIPping is probably also caused by the use of W15Mo and undetected inhomogeneities in the powder. This finding is supported by the fact that no substantial amount of porosity was found by use of subcarbide containing powders for which only C but no W15Mo addition was necessary [12] and a substantial amount of porosity is found if too much Mo2C is added to WC-Co formulations [6,12].

Similar to previous findings, also the use of carburised powders causes grains with a core-rim structure with white-grey (W richer than average) or dark-grey (Mo richer than average) cores, sometimes threefold, which a white-grey core, an inner dark-grey rim and a medium-grey outer rim.

The (W15Mo)C-Co hardmetals have lower fracture toughness (KIC) at the same hardness than WC-10Co system, regardless of the binder phase content. The prepared grades show inhomogeneous microstructures which could stem from a too high free carbon content of the powder (hence, a too high W15Mo addition was necessary) and an unequal distribution of W and Mo in the binder within one series of equal Co content and also among these grades with different Co content. Upon further optimisation, with achieving uniform grain-size distribution, reduction of porosity by use of high-quality hard-phase powder, which makes sense for systematic carbon doping, it can be assumed that the level of WC-Co could be reached. As observed from hardmetals with Mo addition or Mo-rich (W,Mo)C hardmetals, the modified hard phase could give some benefit due to increased TRS, lower friction and the lubrication behaviour of Mo compounds. The spherical, very fine hard-phase (W15Mo)C particles could have positive impact on crack resistance if a uniform microstructure with such particles is achieved.

Acknowledgements

The DTA/TGA investigations were performed at TUTEC GmbH, Vienna.

References