The melting behaviour of pseudobinary (Ti, Mo)C–Co and (Ti, W)C–Co alloys was investigated by thermo-analytical and metallurgical methods including compositional measurements by energy dispersive spectroscopy (EDS). As a result of these investigations with respect to their melting behaviour, it was concluded that the pseudobinary (Ti, Mo)C–Co and (Ti, W)C–Co alloys behave in an analogous way as TiC–Co alloys do. The solidification terminates with a pseudobinary eutectic reaction: melt $C_{0_{ss}} + (Ti, Mo)C$ ($Me = Mo, W$) at an eutectic temperature influenced by the $[Me]/([Ti] + [Me])$ ratio of the alloys. The nature of the starting materials, whether they are carbide mixtures or pre-alloyed carbides, affects neither the phase equilibria nor the solidification behaviour.

**Schmelzverhalten von (Ti, Mo)C–Co und (Ti, W)C–Co-Legierungen**


**1 Introduction**

Although the binary boundary systems have been fairly well established, there appears to exist no comprehensive research work on the quaternary Co–Ti–Mo–C alloy phase diagram. So far only publications [1, 2] on the ternary Co–Ti–C system are available regarding the melting behaviour in the Co corner and the phase equilibria between TiC, $C_{0_{ss}}$ and the (Co–Ti) intermetallic phases. According to Bäckerud et al. the ternary Co–Ti–C system features a ternary eutectic reaction: melt $C_{0_{ss}} + TiC + C$, which is located at about 12.6 at.% C, 4 at.% Ti and 83.4 at.% Co with an eutectic temperature of 1265 ± 5 °C. The liquidus surfaces in equilibrium with cobalt solid solution ($C_{0_{ss}}$), with graphite (C) and with TiC intersect to form melting troughs of two-fold saturation shown in a diagram [1]. The temperature of the pseudobinary eutectic reaction: melt $C_{0_{ss}} + TiC$ was reported to be 1360 °C. The results by Bäckerud have been confirmed by Frey et al. [3]. It has yet not been unequivocally established whether stoichiometric TiC can really form a saddle point with Co resulting a pseudobinary eutectic behaviour or whether the melt in equilibrium with stoichiometric TiC has a composition that is not really on the connecting line between TiC$_{1.0}$ and $C_{0_{ss}}$.

Groschner et al. [4] studied the melting behaviour of the system Co–Mo–C. A Co–rich liquid melt coexists with Mo$_2$C at a composition lying on the connecting line $C_{0_{ss}}$–Mo$_2$C. This line intersects a melting trough that leads to a ternary eutectic with the solid phases Mo$_2$C, $C_{0_{ss}}$–solid solution and graphite (C) being in equilibrium with the liquid phase. The eutectic reaction: melt $C_{0_{ss}} + Mo_2C + C$ takes place at the composition of 69 at.% Co, 18 at.% Mo and 13 at.% C with an eutectic temperature of 1173 ± 9 °C.

The system Co–W–C has been extensively investigated by several authors [5 to 9]. Here, too, the phase WC is co-existent with Co solid solution at temperatures below 1275 °C. The composition of the ternary eutectic WC, C and $C_{0_{ss}}$ has been found to be near 10 at.% W, 11 at.%
Table 1. Compositions and suppliers of starting powders

<table>
<thead>
<tr>
<th>Powder</th>
<th>Composition [in wt.%]</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>&gt; 99.5 Co, &lt; 0.5 O, &lt; 0.2 Ni</td>
<td>H. C. Starck, Germany</td>
</tr>
<tr>
<td>TiC</td>
<td>19.28 C, 0.17 C_{free}</td>
<td>H. C. Starck, Germany</td>
</tr>
<tr>
<td>Mo_2C</td>
<td>5.72 C</td>
<td>H. C. Starck, Germany</td>
</tr>
<tr>
<td>Mo</td>
<td>&gt; 99.7 Mo, &lt; 0.3 O, 0.02 Fe</td>
<td>Metallwerk Plansee, Austria</td>
</tr>
<tr>
<td>(Ti_{0.72}, Mo_{0.28}) Co_{0.86}</td>
<td>&lt; 0.03 C_{free}, 0.2 O, 0.03 Fe</td>
<td>Treibacher Chemische Werke AG, Austria</td>
</tr>
<tr>
<td>WC</td>
<td>582A/79</td>
<td>Wolfframhütte Bergla, Austria.</td>
</tr>
<tr>
<td>Graphite</td>
<td>&lt; 0.01 Fe, &lt; 0.01 Ca &lt; 0.007 S</td>
<td>Lonza, Switzerland</td>
</tr>
</tbody>
</table>

C and 79 at.% Co and the eutectic temperature is about 1275°C.

The Ti-Mo-C and Ti-W-C systems [10, 11] are characterised by an extensive range of solid solutions δ-(Ti, Mo) C_1–x and δ-(Ti, W) C_{1-c}. Quite a significant part of the titanium atoms in the cubic TiC lattice can be replaced by Mo and W atoms without changing the structure of the f.c.c. TiC.

Cutting materials of the type "Cermets" contain relative high proportions of the carbide phase. During liquid phase sintering, most of the carbides remain undissolved. Because of the slow diffusion kinetics, complete equilibrium is impossible to obtain under industrial sintering conditions. It can safely be assumed that the composition of the liquid phase will be in equilibrium with just the surface of the hard particles that remain undissolved. Likewise, the composition of the carbide phase that precipitates epitaxially from the saturated melt upon cooling will be determined by the Ti/Me ratio in the melt. In order to be able to investigate the reactions that are going on during liquid phase sintering, it is necessary to obtain information about these equilibria. In order to facilitate the study, pseudobinary compositions of (Ti_{1-x}, Mo_x) C–Co (x = 0 to 0.6, z = 0.85 and 1 respectively) and (Ti_{1-y}, W_y) C–Co (x = 0 to 0.4) were chosen because the melting behaviour and the phase equilibria in such pseudobinary systems can be considered to correspond to those in industrial cermets. The melting behaviour has been investigated by differential thermal analysis (DTA). The influence of the nature of the starting materials on the melting behaviour either in form of prealloyed carbides or of carbide mixtures was also studied.

2 Experimental Methods

The starting powder materials used in the preparation of the alloys are given in Table 1. Pre-alloyed ternary carbide powders were prepared by heating thoroughly mixed binary carbide powders with or without graphite, depending on the required products, at a temperature of 1900°C for 4 to 12 hours under vacuum of 6 to 8 × 10^-3 mbar. The pre-alloyed ternary carbide powders prepared in this way are very homogeneous as indicated by a clear splitting of the α_1/α_2 diffraction lines in the X-ray diffraction patterns.

The powder mixtures were prepared from the starting materials by weighing and dry mixing in a plastic bottle for 3 to 4 days. The powder mixture was transferred into an alumina crucible for DTA measurements. DTA was carried out in a GTA furnace equipped with a SiC heating tube and a mullite finger tube which can be operated under vacuum or protective atmosphere. In the present study, the mullite tube was evacuated and then back filled with pure Ar (> 99.999% Ar). The heating and cooling rate for all specimens was set at 10 K/min. The maximum experimental temperature is about 1450°C. At this temperature, all samples with the exception of sample TM204 (see Table 2) were completely melted. Several consecutive DTA runs were made for each sample in order to make sure that the results represent true equilibrium conditions. A 25 μm thick zirconium foil served as an oxygen getter. The temperature was measured with a Pt/Pt10%Rh thermocouple and the accuracy of the temperature measurement was estimated to be within ±3 K by calibration against known melting points of highly pure Cu and Cu–Ni alloys.

Fig. 2. Alloy T201, 9.8 mol% TiC–Co. Primary dendritic Co phase and “Chinese script” pseudobinary eutectics without any ternary eutectics.

Fig. 3. Alloy TM205, 9.8 mol% (Ti_{0.8}, Mo_{0.2}) C–Co from mixtures of (Ti_{0.8}, Mo_{0.2}) C and Co. The microstructures are very similar to that of T201.
Table 2. Compositions and melting point intervals of (Ti, Mo) C–Co alloys.

<table>
<thead>
<tr>
<th>Alloy Number</th>
<th>Co at.%</th>
<th>Ti at.%</th>
<th>Mo at.%</th>
<th>C at.%</th>
<th>Pseudobinary eutectic intervals [°C]</th>
<th>Starting materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>T201</td>
<td>82.12</td>
<td>8.94</td>
<td>0</td>
<td>8.94</td>
<td>1362–1407</td>
<td>TiC, Co</td>
</tr>
<tr>
<td>TM8206</td>
<td>82.11</td>
<td>7.16</td>
<td>1.74</td>
<td>8.94</td>
<td>1363–1389</td>
<td>(Ti₉₋₁₂, Mo₀₋₂₅) C₀₈₅</td>
</tr>
<tr>
<td>TM7206</td>
<td>82.15</td>
<td>6.25</td>
<td>2.68</td>
<td>8.93</td>
<td>1362–1389</td>
<td>Mo₂C, C, Co</td>
</tr>
<tr>
<td>TM6206</td>
<td>82.15</td>
<td>5.35</td>
<td>3.57</td>
<td>8.92</td>
<td>1338–1383</td>
<td>TiC, Mo₂C, C, Co</td>
</tr>
<tr>
<td>TM5206</td>
<td>82.20</td>
<td>4.45</td>
<td>4.45</td>
<td>8.90</td>
<td>1347–1371</td>
<td>(Ti₁₋₄, Mo₀₋₁₇) C, Co</td>
</tr>
<tr>
<td>TM4206</td>
<td>82.18</td>
<td>3.56</td>
<td>5.35</td>
<td>8.91</td>
<td>1335–1363</td>
<td>(Tiₒ₋₁₂, Moₒ₋₄₈) C₀₈₅, Co</td>
</tr>
<tr>
<td>TM9205</td>
<td>82.10</td>
<td>8.05</td>
<td>0.90</td>
<td>8.95</td>
<td>1366–1387</td>
<td>(Tiₒ₋₁₂, Moₒ₋₄₈) C₀₈₅, Co</td>
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<tr>
<td>TM8205</td>
<td>82.09</td>
<td>7.17</td>
<td>1.79</td>
<td>8.96</td>
<td>1367–1391</td>
<td>(Tiₒ₋₁₂, Moₒ₋₄₈) C₀₈₅, Co</td>
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<tr>
<td>TM7205</td>
<td>82.14</td>
<td>6.25</td>
<td>2.68</td>
<td>8.93</td>
<td>1366–1390</td>
<td>(Tiₒ₋₁₂, Moₒ₋₄₈) C₀₈₅, Co</td>
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<tr>
<td>TM8204</td>
<td>47.29</td>
<td>21.09</td>
<td>5.27</td>
<td>26.56</td>
<td>1362–1387</td>
<td>(Tiₒ₋₁₂, Moₒ₋₄₈) C₀₈₅, Co</td>
</tr>
<tr>
<td>TM6205A</td>
<td>83.59</td>
<td>4.61</td>
<td>4.26</td>
<td>7.55</td>
<td>1354–1383</td>
<td>(Tiₒ₋₁₂, Moₒ₋₄₈) C₀₈₅, Co</td>
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<tr>
<td>TM5206S</td>
<td>83.28</td>
<td>4.51</td>
<td>4.51</td>
<td>7.69</td>
<td>1346–1376</td>
<td>(Tiₒ₋₁₂, Moₒ₋₄₈) C₀₈₅, Co</td>
</tr>
<tr>
<td>TM4206S</td>
<td>83.28</td>
<td>3.61</td>
<td>5.42</td>
<td>7.70</td>
<td>1338–1368</td>
<td>(Tiₒ₋₁₂, Moₒ₋₄₈) C₀₈₅, Co</td>
</tr>
</tbody>
</table>

After the DTA measurements the solidified samples were cut with a diamond wheel, embedded in resin, ground with a diamond disk (20 μm) followed by SiC paper (2500 mesh) and 3 μm diamond paste and finally polished with an aqueous silica suspension. Polished sections of the alloys were investigated in an optical microscope (Leitz MM6) and a scanning electron microscope (JEOL JSM 6400) equipped with an energy dispersive spectroscopy (EDS) detector for compositional analysis.

3 Results

3.1 The Pseudobinary (Ti, Mo) C–Co Alloys

The thermal effects accompanying the solid-liquid phase reactions were recorded by differential thermal analysis (DTA). The results are shown in Table 2. The usual set-up of DTA makes it impossible to distinguish unambiguously between reactions comprising a liquid phase and one, two or three solid phases because of the insufficient heat conductivity of the alumina crucible of the system, particularly with the thermal effects being in rather small temperature ranges in the present case. The measurements led to the conclusion that only one eutectic reaction takes place for each studied alloy. The melting point of the alloy T201 with the composition of 9.8 mol% TiC and 90.2 mol% Co was determined to be 1362 °C, which is consistent with the temperature of 1360 °C reported by Bückel et al. [1] for the pseudobinary eutectic reaction: melt Co₉₀₅ + TiC.

The influence of the Mo content in (Tiₒ₋₁₂, Moₒ₋₄₈) C on the melting behaviour is shown in Fig. 1. With increasing [Mo]/[(Ti) + (Mo)] ratio of the starting carbides (Tiₒ₋₁₂, Moₒ₋₄₈) C with x values from 0 to 0.6, the melting points of the alloys with 9.8 mol% (Tiₒ₋₁₂, Moₒ₋₄₈) C and 90.2 mol% Co do not change significantly if x ≤ 0.4 and decrease from 1358 °C to 1335 °C if x increases from 0.4 to 0.6.

Similarly to the behaviour within the Ni–Ti–Mo–C system [12], the nature of the starting materials, whether they are mixtures of binary carbides (TiC, Mo₂C and C), or mixtures of a pre-allloyed carbide (Tiₒ₋₁₂, Moₒ₋₄₈) C₀₈₅, with Mo₂C and C, or pre-allloyed (Tiₒ₋₁₂, Moₒ₋₄₈) C, does not affect the melting points of the (Ti, Mo) C–Co alloys if the gross compositions of the alloys are the same. On the other hand, the stoichiometry factor x, which has a considerable influence on the melting points of the (Ti, Mo) C–CoNi alloys, nearly does not influence the melting points of the (Ti, Mo) C–Co alloys in the studied compositional ranges. For instance, the melting point of TM5206 which contains the stoichiometric carbide (Tiₒ₋₁₂, Moₒ₋₄₈) C is 1347 °C, whilst that of TM5206S which has a sub-stoichiometric carbide (Tiₒ₋₁₂, Moₒ₋₄₈) C₀₈₅ is 1346 °C.

![Fig. 4. Alloy TM5206, 9.8 mol% (Tiₒ₋₁₂, Moₒ₋₄₈) C–Co from mixtures of Mo₂C, (Tiₒ₋₁₂, Moₒ₋₄₈) C₀₈₅, C and Co.](image1)

![Fig. 5. Alloy TM5206S, 9.8 mol% (Tiₒ₋₁₂, Moₒ₋₄₈) C₀₈₅–Co from mixtures of (Tiₒ₋₁₂, Moₒ₋₄₈) C₀₈₅ and C. Primary Co phase and binary eutectics without any ternary eutectic phase.](image2)

![Fig. 6. Alloy TM8204, 65 mol% (Tiₒ₋₁₂, Moₒ₋₄₈) C–Co from mixtures of (Tiₒ₋₁₂, Moₒ₋₄₈) C and Co. "Core-shell" structure carbides in the Co matrix, BSE image.](image3)
All DTA alloys containing 90.2 mol% Co feature nearly identical microstructures. Beside the primary dendritic Co phase, there is a pseudobinary eutectic constituent with “Chinese script” characteristics (see Fig. 2 to Fig. 5). The microstructure of the ternary alloy T201 with a composition of 9.8 mol% TiC and 90.2 mol% Co is shown in Fig. 2. After the solidification of primary Co crystals, the solidification terminates with the pseudobinary eutectic reaction: melt Co$_{90.2}$ + TiC at a temperature of 1362°C.

During solidification, the quaternary (Ti, Mo) C–Co alloys with about 10 mol% (Ti, Mo) C develop microstructures very similar to that of the ternary alloy T201. And furthermore, the alloy status of the starting material as well as the carbon content (in the range of stoichiometric factor of 0.85 to 1) do not affect the microstructures. For instance, both alloys, TM8205 (prepared from pre-alloyed carbide (Ti$_{0.8}$, Mo$_{0.2}$) C) and TM5206 (prepared from mixtures of carbides TiC, Mo$_2$C and C), have the same microstructures as shown in Fig. 3 and Fig. 4. The microstructure of the alloy TM5206S with a sub-stoichiometric carbide is very much the same as that of the alloy TM5206 as illustrated in Fig. 5. In all these cases, the solidification starts with the precipitation of a primary dendritic Co phase and terminates with the pseudobinary eutectic reaction: melt Co$_{90.2}$ + (Ti, Mo) C.

In the present investigations, the characteristic microstructures corresponding to the ternary eutectic reactions: melt Co$_{90.2}$ + TiC + C and melt Co$_{90.2}$ + (Ti, Mo) C + C were observed neither in the ternary alloy T201 nor in the 9.8 mol% (Ti$_{1-x}$, Mo$_{x}$C–90.2 mol% Co quaternary alloys.

The microstructures of DTA alloys with about 65 mol% Co are very different from those of the alloys with 90.2 mol% Co. Although the pseudobinary eutectic reactions: melt Co$_{90.2}$ + (Ti, Mo) C did give rise to the pertinent thermal effects in DTA runs (see Table 2), no binary eutectic microstructure could be observed (see Fig. 6). Only two constituents, carbide particles and cobalt solid solution, have been observed in the microstructures of alloy TM8204 as shown in Fig. 6. Evidently, in such cases as TM8204 with a carbide content exceeding the solubility limit for the highest experimental temperature, some carbide particles remain undissolved at the temperature of the eutectic reaction. As the temperature decreases from the maximum temperature, dissolved (Ti, Mo) C re-precipitates from the Co liquid and grows on the undissolved nuclei to form the “core-rim” structure within the carbide phase. The solidification continues and terminates with the pseudobinary eutectic reaction: melt Co$_{90.2}$ + (Ti, Mo) C at a temperature of 1362°C. During the eutectic reaction, the (Ti, Mo) C phase precipitates epitaxially around the undissolved carbide grains so that the typical eutectic feature does not appear in the microstructure.

The compositions of the pseudobinary microstructural eutectic regions were measured by SEM/EDS area scanning. In the ternary Co–Ti–C alloy T201 the pseudobinary eutectic constituent has a composition of ~11 mol% TiC. Incidentally, in the (Ti, Mo) C–Co alloys, the pseudobinary eutectic regions do also have a composition of ~11 mol% (Ti, Mo) C. Even in the alloy TM6205A, which had been prepared from a sub-stoichiometric carbide (Ti$_{0.8}$, Mo$_{0.2}$) C$_{0.85}$, the pseudobinary eutectic constituent contains ~11 mol% (Ti, Mo) C, too.

When DTA specimens were cut along their longitudinal sections (parallel to the direction of the force of gravity), an inhomogeneous microstructure was found in each specimen. An example is given in Fig. 7 where a primary Co phase and a pseudobinary eutectic constituent can only be observed at the bottom of the specimen. On top of the sample there is no pseudobinary eutectic microstructure but blocky carbides with “core-rim” structures embedded in a Co matrix. It was observed that the pseudobinary eutectic carbide constituent in the lower part of the specimen was very homogeneous without any “core-rim” structure but the blocky carbides at the top of the specimen did have a typical “core-rim” feature (see Fig. 8 and Fig. 9). The difference in the microstructures across the longitudinal section could be due to the effect of gravity. The density of TiC is 4.93 g/cm$^3$, which is relatively low compared with cobalt melt (~8.9 g/cm$^3$). If TiC is not immediately dissolved after melting has set in or if Mo poorer (Ti, Mo)
C particles remain undissolved because of preferential dissolution of Mo in the Co melt, then TiC particles may float upwards and thus lead to a concentration gradient within a DTA ingot. A random region on the top of the sample TM8205 was measured by SEM/EDS area-scanning and the \([\text{Mo}/(\text{Ti} + \text{Mo})] = 0.126\) ratio was lower than in the original alloy with \([\text{Mo}/(\text{Ti} + \text{Mo})] = 0.2\).

3.2 Pseudobinary (Ti, W) C–Co Alloys

Quaternary Co–Ti–W–C alloys are extensively used as hardmetals for metal cutting with WC and (Ti, W) C as hard phases and Co as binder phase. However, most work focused on the ternary system Co–W–C rather than on the Co–Ti–W–C quaternary system.

DTA experiments were performed for some alloys with the compositions of 9.8 mol% mixed carbides \((\text{Ti}_{10} \text{W}_2)\) C and 90.2 mol% Co \((x = 0.1, 0.2, 0.3, 0.4\), respectively). The normal compositions, the thermal signals of DTA and the starting materials of these alloys are given in Table 3.

The melting points of the alloys increase from 1362 °C to 1381 °C with increasing \([\text{W}/(\text{Ti} + \text{W})]\) atom ratios of the starting carbides from 0 to 0.4. Figure 10 gives a graph of the onset of the melting temperatures as a function of the composition of the starting carbide.

Microstructures of the DTA alloys with different W contents are very similar. An example is given in Fig. 11. A primary Co dendrite and a “Chinese script” pseudobinary eutectic constituent are observed in the optical microscope. There are a few polygonal blocky carbides in the microstructure, too. The solidification starts with the development of primary Co(Co) dendrites and terminates with the pseudobinary eutectic reaction: melt Co(Co) + (Ti, W) C. The features of the ternary eutectic reaction: melt Co(Co) + (Ti, W) C + C have not been observed in analogy to the situation in (Ti, Mo) C–Co alloys.

4 Conclusions

The melting behaviour of the pseudobinary (Ti, Mo) C–Co and (Ti, W) C–Co alloys apparently do show the same characteristics as those of the TiC–Co alloys, and furthermore, they can be treated in a manner analogous to a pseudo-ternary system comprising the components of Co, TiC and “MoC” (or WC) as illustrated in Fig. 12. Within the compositional areas of the present study, the solidification of alloys within the pseudobinary systems (Ti, Me) C–Co (Me = Mo or W) starts with the primary precipitation of either Co(Co) or carbide phase (Ti, Me) C and ends with the pseudobinary eutectic reaction: melt Co(Co) + (Ti, Me) C. The pseudo-ternary eutectic reaction: melt Co(Co) + (Ti, Me) C + C has not been observed probably due to carbon contents in the alloys being insufficient to lead to graphite precipitation (stoichiometric factor of the alloys studied: C/(Ti, Me) ≤ 1).

The pseudobinary eutectic temperatures of the reaction: melt Co(Co) + (Ti, Me) C are a function of the [Me]/[Ti] + [Me] ratio of the alloys. The nature of the starting materials, whether they are carbide mixtures of the binary carbides with Co or whether they are pre-alloyed carbides with Co,
do not show any influence on the melting behaviour. SEM/EDS measurements indicate that the composition of the pseudobinary eutectics in (Ti, Me) C–Co alloy systems are situated at a molar ratio near 10 mol% carbide phase and 90 mol% Co as similar to the location of the pseudobinary eutectic in the TiC–Co alloy.

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### Literature


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