

Experimental Study of Invariant Equilibria in the Co-W-C and Co-W-C-Me (Me = Ti, Ta, Nb) Systems

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New experimental information on liquid/solid invariant equilibria in systems of importance for cemented carbides has been generated using a differential thermal analysis (DTA) technique. The temperatures of the invariant equilibria $\text{liq} + \text{fcc-Co} + \text{WC} + \text{graphite}$ and $\text{liq} + \text{fcc-Co} + \text{WC} + \text{M}_6\text{C}$ have been determined for the Co-W-C system. For the Co-W-C-Me systems, where Me is a cubic carbide forming metal (Ti, Ta, or Nb), the corresponding temperatures of the invariant equilibria, including the cubic carbide phase, have been measured. The compositions of the M_6C phase and the cubic carbide after rapid cooling from 1400 °C have been determined by electron probe microanalysis. The M_6C phase was found to accept Ta or Nb on its W position, whereas the acceptance of Ti was negligible. The measured solubility of W in Ti-based cubic carbide was in good agreement with previous determinations. However, the W solubility was found to be considerably lower for Ta- and Nb-based cubic carbide compared to data reported in the literature.

Introduction

Cemented carbides are produced by liquid phase sintering and consist of grains of hard hexagonal WC embedded in a more ductile binder phase, usually based on Co. Often, other hard phase grains are present in the form of carbides and nitrides with a cubic structure. The metal composition of the cubic phase may vary over a wide range but is often a mixture of W, Ti, Ta, and Nb. The hard grains range in size from submicron to several micrometers. The relative amount of binder phase is rather low, typically less than 15 vol.%.

A recognized tool in alloy and process development is phase equilibria calculations based on modeling of the thermodynamic properties of the phases that may form in the system, the so-called CALPHAD method [1970Kau, 1998Sau]. For example, the formation of a tough surface zone during sintering has successfully been simulated as consisting of multicomponent diffusion coupled with thermodynamic considerations [2000Ekr]. Such a surface zone is enriched in binder phase and depleted in cubic carbonitrides.

The carbon balance of cemented carbides must be carefully controlled. If the carbon content is too high, then free graphite will form. A too low carbon content will result in formation of M_6C carbide with composition often given as $\text{Co}_3\text{W}_3\text{C}$. Both graphite and M_6C are unwanted because they cause brittleness in the cemented carbide. The liquidus and solidus temperatures are also of importance, *e.g.*, when designing the sintering cycle. Accurate experimental information on the temperatures of relevant invariant liquid/solid equilibria in combination with thermodynamic modeling can provide very precise predictions of how liquidus and solidus temperatures vary with composition.

The invariant equilibria of main interest in the Co-W-C

system are $\text{liq} + \text{fcc-Co} + \text{WC} + \text{graphite}$ and $\text{liq} + \text{fcc-Co} + \text{WC} + \text{M}_6\text{C}$. For Co-W-C-Me systems, where Me is a cubic carbide forming metal, the corresponding invariant equilibria will also include the cubic carbide phase.

Despite the industrial importance of cemented carbides, the phase diagrams and the thermodynamic properties are not well established. The purpose of the present work is to generate new experimental information, which will contribute to a more accurate and reliable model description of the thermodynamic properties of systems of relevance for cemented carbides.

Experimental Procedures

Chemical compositions for the experimental runs were chosen so that either free graphite or M_6C phase was present at the invariant equilibrium $\text{liq} + \text{fcc-Co} + \text{WC} + (\text{cubic carbide}) + \text{graphite}/\text{M}_6\text{C}$ phase. The presence of cubic carbide phase was accomplished by including TiC, TaC, or NbC in the original sample mixture. Carbon concentrations were chosen to allow for minor loss or gain of carbon *via* furnace atmosphere without risk of crossing phase boundaries. Because nucleation of solid WC from the binder phase melt is difficult, the proportion of WC in samples was large in order to keep part of the WC in the solid state at all temperatures.

The raw materials used in the experiments were the same as in hard metal production. The qualities were WC DS80S from H.C. Starck, W metal W-600 from Seco Tools AB, Co extra fine from OMG Kokkola, and Cabot carbon black. TiC as (W,Ti)C, TaC, and NbC were produced by H.C. Starck. Apart from O contents in the range 0.05 to 0.2 wt.%, the impurity in metals and carbides was mainly Fe (range ≤ 0.001 to 0.02 wt.%). The Co contained 0.0047 wt.% Ni and the NbC 0.51 wt.% Ta. The TiC and TaC contained 0.18 and 0.01 wt.% N, respectively. The appropriate relative amounts of constituents were computed and weighed for each experiment. The raw material, with a total weight of a few tens of

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grams, was put into a plastic jar and then mixed for at least 2 h in a Turbula mixer. From this mixture, a sample of approximately 130 to 140 mg was taken for differential scanning calorimeter (DSC) runs.

Thermal analysis was performed in a Setaram (Caluire, France) 92-16.18 thermoanalyzer equipped with a DSC 1500 °C rod. The crucible containing the sample was closed with a lid in order to reduce any interaction between sample and furnace atmosphere. Samples were cycled ten times between 1250 and 1400 °C at a rate of 2 °C/min in an atmosphere of slowly flowing argon. After cycling, the samples were held at 1400 °C for 1 h; temperature was then decreased to room temperature initially by 90 °C/min. The measured temperature variation during the isothermal run was less than ± 1 °C.

The equipment for reading temperature was calibrated by melting pure Co (rod, 99.998% pure, Johnson Matthey (Västra Frölunda, Sweden)) with excess carbon at the same heating rate as in measurements. The reading was then compared with the value assessed for the eutectic temperature of the Co-C system, 1321 °C, by Guillermet [1989Gui]. Two sets of experimental runs were made: with alumina crucibles for equilibria with M_6C phase present and graphite crucibles for equilibria with graphite. For each set, one calibration was made using the same crucible material as in runs. For each set, two runs were made followed by calibration and then two more runs were made. In both calibrations, the measured value was 1319 °C and hence the correction was found to be +2 °C.

Samples were picked out of the crucible after each experiment. Polished sections were prepared and phases identified by scanning electron microscopy/energy dispersive spectroscopy in order to confirm that the intended phase assembly was present during thermal analysis. Further analysis of phase compositions was then made by electron probe microanalysis (EPMA) using a JEOL JXA8900R combined wavelength and energy dispersive microanalyzer (Japan Electron Optics Ltd., Tokyo).

Results and Discussion

Attempts to determine melting point onset temperatures from raw data using the thermoanalyzer software gave results that were obviously erroneous. Every single melt event therefore was plotted on paper as a heat flow versus temperature diagram, and the recorded onset temperature was defined as the ruler-and-pencil intersection between the extrapolated base line and the endotherm peak onset leg. For each one of the samples, ten melt events were thus recorded and onset temperatures determined. The first events often gave temperatures that radically differed from the following ones and were hence excluded as nonequilibrium melting. The remaining nine equilibrium temperatures per sample were then corrected by the value obtained in the calibration procedure.

The mean values for the invariant equilibria from the differential thermal analysis (DTA) experiments are given in Table 1. A summary of suggested literature values for the temperatures of the two studied invariant equilibria in the Co-W-C system is given in Table 2. The suggestions are

Table 1 Temperatures of invariant solid/liquid equilibria including WC, (cubic carbide), and graphite or M_6C . The freezing point depression ΔT for the equilibria when adding Ti, Ta, or Nb is also given

System	Invariant T (°C) graphite	Invariant T (°C) M_6C	ΔT (°C) graphite	ΔT (°C) M_6C
Co-W-C	1298	1368
+Ti	1289	1361	-9	-7
+Ta	1289	1352	-9	-16
+Nb	1282	1345	-16	-23

based on DTA experiments, solidification studies, and thermodynamic analyses. Note that the temperatures presented here are in good agreement with the experiments by Rautala and Norton [1952Rau].

The most extensive evaluation of the Co-W-C system is due to Guillermet [1989Gui], who applied the CALPHAD method to assess the thermodynamic properties of most of the phases in the system. The majority of available experimental information was satisfactorily accounted for. However, there was only a small amount of contradictory information available concerning the liquidus surface. Guillermet, therefore, decided to consider only the temperature for the liq + fcc-Co + WC + graphite equilibrium reported by Åkesson [1982Åke] in the optimization. The rest of the calculated liquidus surface is controlled by a combination of all the other experimental data and the applied thermodynamic models. It is known that nucleation of WC from a melt is quite sluggish. A possible explanation for the reported lower liquidus temperatures by Åkesson [1982Åke] is that they were due to the absence of WC nucleation during sample cooling, so the temperature of the metastable equilibrium liquid + fcc-Co + M_6C + graphite equilibrium would be determined instead of the anticipated liquid + fcc-Co + WC + graphite.

No experimental information on the temperatures of invariant liquid/solid equilibria for Co-W-C-Me systems was found in the literature. The solubilities of the Me elements studied here are very low in the solid fcc-Co phase [1975Jon]. It can thus be assumed that the relation $\Delta T = \text{constant} \cdot x$ can be applied; *i.e.*, the freezing point depression ΔT of invariant solid/liquid equilibria when adding a cubic carbide phase is proportional to the solubility x in mol fraction of the carbide-forming metal element in the liquid. The solubilities of Ti and Ta are hence approximately equal at the invariant equilibrium including graphite, while the solubility of Nb is about twice as large (Table 1). The freezing point depression is about the same for the two invariant equilibria including graphite and M_6C phase when adding Ti. The freezing point depression when adding Ta or Nb is higher for the M_6C equilibrium compared to the graphite equilibrium.

The compositions of the M_6C phase after rapid cooling from 1400 °C measured by EPMA are given in Table 3. The generally accepted stoichiometric formula for the M_6C carbide in the Co-W-C system, Co_3W_3C , corresponds to the following composition in weight percent: 1.61% C, 23.9% Co, and 74.5% W. Thus, the EPMA measurement somewhat overestimates the C content, but the accuracy for the metallic

Table 2 Temperatures for the studied invariant equilibria in the Co-W-C system according to the present work and various sources

Equilibrium	T (°C)	Ref	Method
Liq + fcc-Co + WC + graphite	1300	[1952Rau]	DTA
	1255	[1976Uhr]	Solidification, modeling
	1245–1300	[1977Joh]	Solidification
	1275	[1982Åke]	Rapid solidification and modeling
	1276	[1984Gab]	Modeling
	1275	[1989Gui]	Modeling
	1298	Present work	DTA
Liq + fcc-Co + WC + M ₆ C	1359	[1952Rau]	DTA
	1320	[1976Uhr]	Solidification studies, modeling
	1300–1400	[1977Joh]	Solidification
	1355	[1982Åke]	Modeling
	1304	[1984Gab]	Modeling
	1326	[1989Gui]	Modeling
	1368	Present work	DTA

Table 3 Composition of the M₆C phase in weight percent measured by EPMA after rapid cooling from 1400 °C. Resulting formulas are computed assuming a general M₆C stoichiometry

System	%C	%Co	%Ti	%Ta	%Nb	%W	Formula
Co-W-C	1.93	24.6	73.4	Co _{3.07} W _{2.93} C
+Ti	1.92	23.2	0.3	73.2	Co _{2.96} W _{2.99} Ti _{0.05} C
+Ta	1.98	24.3	...	5.4	...	68.3	Co _{3.04} W _{2.74} Ta _{0.22} C
+Nb	2.06	24.7	2.0	71.2	Co _{3.04} W _{2.81} Nb _{0.16} C

elements is fairly good. The measured solubility of Ti in the M₆C phase is low and within the uncertainty of the method. Thus, the solubility of Ti in the Co-W based M₆C phase can probably be neglected. However, the measured solubilities of Ta and Nb are significant and should be considered when assessing thermodynamic properties. These elements seemingly prefer to replace W in the structure, whereas the Co content is unaffected. In a transmission electron microscopy/energy dispersive x-ray (TEM/EDX) study of the M₆C phase in a (W,Ti,Ta,Mo)(C, N)-(Co,Ni) cermet, Zackrisson and Andrén [1999Zac] measured higher concentrations of Ti: 4 at.% of the metal content, corresponding to Ti_{0.24} in an M₆C formula.

Results of EPMA analyses of the compositions of cubic carbides are given in Table 4. A low Co content was measured in all samples. The Co signal probably originated from Co in the Co-rich binder phase. The calculated formulas for the cubic carbide phase neglecting the measured Co content and assuming a general MC stoichiometry are also given. The solubility of WC in Ti-based cubic carbide is 0.35 expressed as mol fraction when graphite is present in the sample. This value is in excellent agreement with extrapolations to lower temperatures by Uhrenius [1984Uhr] of the experimental data by Rudy [1973Rud] and with the determined value at 1450 °C by Chatfield [1986Cha]. The measured solubility of WC in TaC at the carbon activity of unity, mol fraction of 0.04, is lower than what is suggested by extrapolation of high temperature data by Rudy [1966Rud] and the experimental

Table 4 Composition of cubic carbide in weight percent measured by EPMA after rapid cooling from 1400 °C for Me = Ti, Ta, or Nb. Data for the equilibria including M₆C or graphite are given for each Me. Resulting formulas are computed neglecting Co and assuming a general MC stoichiometry

System	%C	%Co	%Ti	%Ta	%Nb	%W	Formula
Ti/M ₆ C	9.99	2.1	24.7	63.2	W _{0.40} Ti _{0.60} C
Ti/graphite	12.20	3.1	28.0	56.7	W _{0.35} Ti _{0.65} C
Ta/M ₆ C	5.84	1.8	...	87.5	...	4.9	W _{0.05} Ta _{0.95} C
Ta/graphite	5.85	0.6	...	89.5	...	4.0	W _{0.04} Ta _{0.96} C
Nb/M ₆ C	7.88	1.7	76.4	14.0	W _{0.05} Nb _{0.91} C
Nb/graphite	7.86	0.8	81.2	10.2	W _{0.06} Nb _{0.94} C

value of 0.10 at 1450 °C determined by Chatfield [1983Cha]. The solubility of WC in NbC at graphite saturation determined in the present work, 0.06, is lower compared to the value of 0.12 at 1450 °C by Chatfield [1986Cha] and extrapolations to lower temperatures of experimental data by Rudy [1969Rud].

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