



# Experimental study of carbides in the Ti–Cr–C system

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## ABSTRACT

The Ti–Cr–C system has been studied by producing samples within the MC–M<sub>3</sub>C<sub>2</sub>–M<sub>7</sub>C<sub>3</sub> (M = Ti, Cr) and MC–M<sub>3</sub>C<sub>2</sub>–graphite equilibria. The main purpose was to determine the solubility of Cr in MC; however, the solubility of Ti in M<sub>3</sub>C<sub>2</sub> and M<sub>7</sub>C<sub>3</sub> was also of interest, as well as the C content in MC. Heat treatments have been performed at 1673 and 1773 K for 300 h. Thereafter, the phase compositions have been measured with energy-dispersive X-ray spectroscopy (EDS) and wavelength-dispersive X-ray spectroscopy (WDS). X-ray diffraction (XRD), in combination with Rietveld refinement, has been used to determine the lattice parameter for MC. Density functional theory (DFT) calculations were performed to estimate the lattice parameter for MC as a function of composition, and the Rietveld refined lattice parameters for MC have then been recalculated to compositions in order to verify the EDS measurements. The results show that the EDS and XRD measurements give equal results. One conclusion is that, with the current conditions, 300 h is a sufficient heat treatment time in order to reach thermodynamic equilibrium. The other main conclusion is that the solubility of Cr in MC, in general, was overestimated by previous studies due to too short heat treatment times, but also that the solubility is very temperature dependent, especially for the MC–M<sub>3</sub>C<sub>2</sub>–graphite equilibrium. This clear temperature dependence was not taken into account in the existing thermodynamic description found in the literature.

## Introduction

In the process of finding new and improved cemented carbide grades, the addition of alloying elements becomes increasingly important. To design a new cemented carbide grade, it is important to be able to

predict the stable phases in the produced cemented carbide. Therefore, it is essential to know not only how alloying elements interact with cemented carbide base elements, such as W, Co and C, but also how they interact with each other. Two frequently used alloying elements are Cr and Ti, and their interaction with their respective carbides is thus of

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high importance. Especially the solubility of Cr in TiC, but also the solubility of Ti in  $\text{Cr}_3\text{C}_2$  and  $\text{Cr}_7\text{C}_3$  are of interest. From a thermodynamic modelling point of view, this means that the equilibria  $\text{MC}-\text{M}_3\text{C}_2-\text{M}_7\text{C}_3$  and  $\text{MC}-\text{M}_3\text{C}_2$ -graphite ( $\text{M} = \text{Cr}, \text{Ti}$ ) in the Ti–Cr–C system have to be well described.

Previous studies of these equilibria report somewhat diverging results, but the heat treatment time used in order to reach equilibria was also different. Booker et al. [1] performed an extensive experimental study of the Ti–Cr–C system. With an equilibration time of 40 h, they found the solubility of Cr in MC to be 20.7 at.% for the equilibrium  $\text{MC}-\text{M}_3\text{C}_2-\text{M}_7\text{C}_3$  and 22.8 at.% for the equilibrium  $\text{MC}-\text{M}_3\text{C}_2$ -graphite, at 1773 K. However, He [2] used an equilibration time of 100 h and found the solubilities, at the same temperature, to be much lower, 13.09 at.% and 16.79 at.%, respectively. Ehrenborg [3] increased the equilibration time even more, to 150 h, and found the solubility of Cr in MC to be 8.06 at.% for the equilibrium  $\text{MC}-\text{M}_3\text{C}_2-\text{M}_7\text{C}_3$ , at 1673 K. These results indicate that the solubilities reported by Booker et al. [1] were overestimated due to a too short equilibration time, but it also raises the question whether 100 h or even 150 h, as used by He [2] and Ehrenborg [3], respectively, is enough to reach full thermodynamic equilibrium.

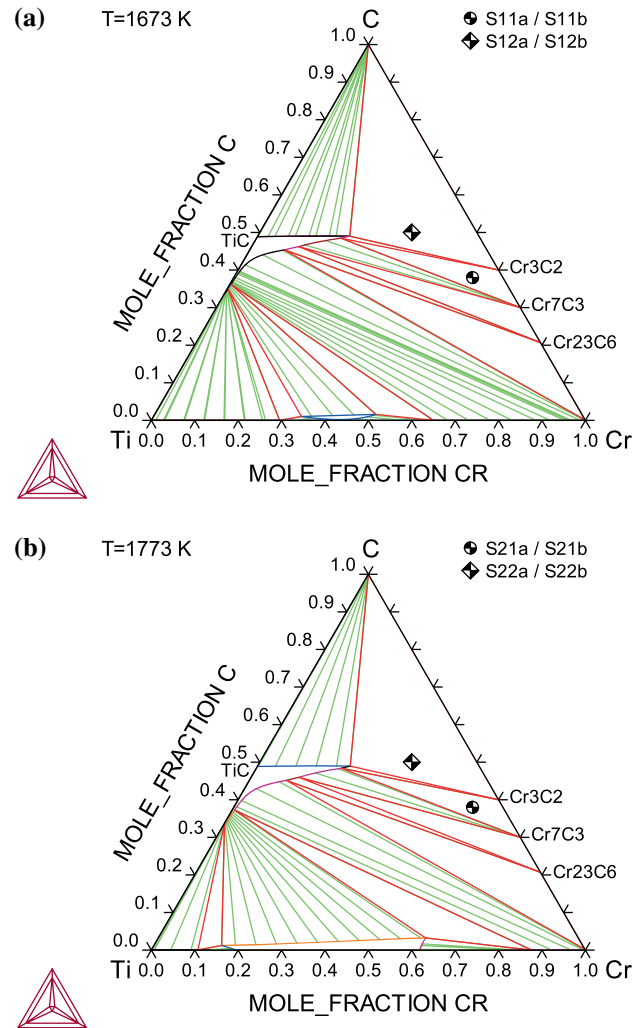
In this work, the equilibria  $\text{MC}-\text{M}_3\text{C}_2-\text{M}_7\text{C}_3$  and  $\text{MC}-\text{M}_3\text{C}_2$ -graphite have been studied at 1673 and 1773 K. The main purpose was to determine the solubility of Cr in MC, but the solubility of Ti in  $\text{M}_3\text{C}_2$  and  $\text{M}_7\text{C}_3$  was also of interest, as well as the C content in MC. An heat treatment time of 300 h was used and in order to verify that equilibrium was reached, two samples with two different sets of raw materials, but with the same total composition, were made for each equilibrium. Cr and Ti contents for each phase have been measured with energy-dispersive X-ray spectroscopy (EDS), C contents with wavelength-dispersive X-ray spectroscopy (WDS), and the solubilities of Cr in MC have been verified with XRD measurements in combination with Rietveld refinement.

Preliminary results from the experiments at 1673 K have been published before by Haglöf et al. [4], but in the present work certified standards (Appendices A and B) have been used as references for the EDS/WDS measurements, 10 grains per phase have been measured instead of three to get better statistics, and

the XRD measurements have been added for verification.

## Method

All thermodynamic calculations in this work were performed using the Thermo-Calc Software [5] together with the thermodynamic description of the Ti–Cr–C system by Schuster et al. [6]. Suitable alloy compositions for the experiments were based on the calculations of the isothermal sections at 1673 and 1773 K (Fig. 1). Two samples were made for each equilibrium (Table 1), where both samples had the same overall composition but were made with different sets of raw materials. The purpose of this was



**Figure 1** Ti–Cr–C isothermal sections according to the description by Schuster et al. [6] at 1673 K (a) and 1773 K (b). Markers show composition of samples in this study.

**Table 1** Ti–Cr–C samples

Sample 1673 K/1773 K	Equilibrium	Ti (at.%)	Cr (at.%)	C (at.%)	Raw materials*
S11a/S21a	MC–M <sub>3</sub> C <sub>2</sub> –M <sub>7</sub> C <sub>3</sub>	7	55	38	TiC, Cr, Cr <sub>3</sub> C <sub>2</sub>
S11b/S21b	–	–	–	–	TiC, Cr <sub>7</sub> C <sub>3</sub> , carbon black
S12a/S22a	MC–M <sub>3</sub> C <sub>2</sub> –Graph.	15	35	50	TiC, Cr, carbon black
S12b/S22b	–	–	–	–	TiC, Cr <sub>7</sub> C <sub>3</sub> , carbon black

\*Carbon black compensation for oxide reduction excluded

to use different reaction paths to reach the equilibrium state. If both samples end up with the same phases and phase compositions, it would strengthen the assumption that equilibrium has been reached.

### Sample synthesis

All the samples were produced as follows:

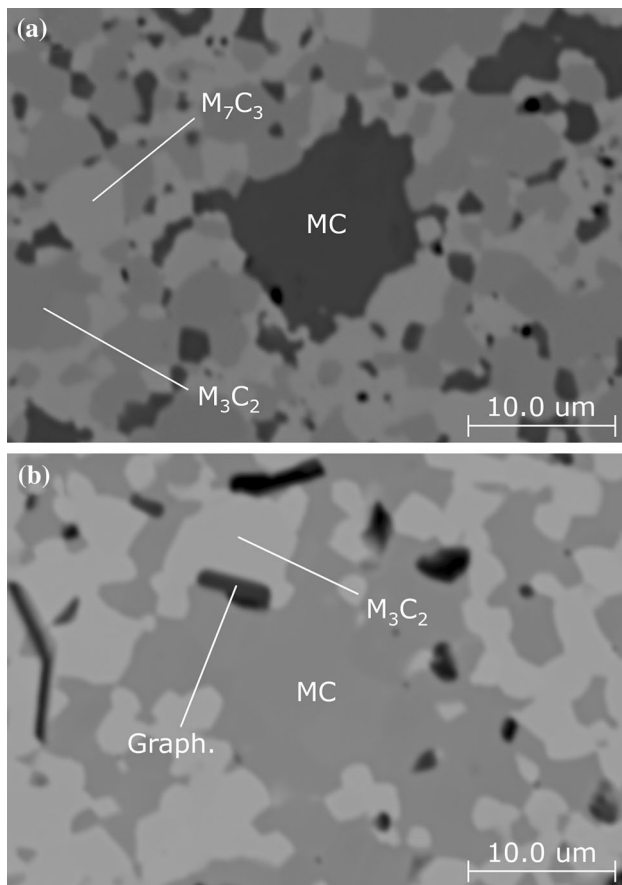
1. Dry mixing the raw materials for 4 h in cylindrical plastic containers using a multi-axial shaker. In order to avoid O, C and other types of contamination as far as possible, no additives (e.g. wax, PEG) or milling bodies were used. Extra carbon black was added to compensate for the impurity level of O in the raw materials (up to 0.8 wt% in the metallic Cr raw material) by assuming that all O would form CO during the heat treatment.
2. Hot pressing to  $\varnothing 10 \times 3$  mm cylindrical samples at 80 MPa in vacuum atmosphere with 20 min holding time at the same temperature as the equilibration temperature. Graphite tools were used, and the graphite stamps were covered with graphite foil. Graphite foil that adhered to the samples was mechanically removed before the subsequent heat treatment.
3. Heat treatment for 300 h in 1 atm stationary Ar atmosphere at 1673 and 1773 K, respectively, in a furnace with graphite insulation and graphite heating elements. Samples were placed on alumina plates. Before the heat treatment, the temperature was calibrated with ceramic process temperature control rings (PTCR) for one hour in a N<sub>2</sub> atmosphere. The result of the PTCRs was also validated by controlling whether samples of pure Ni with a melting point of 1728 K [7] melted or not, during this calibration.

### Sample preparation

The heat-treated samples were cleaned in ethanol in a ultrasonic bath and then hot mounted in a resin, containing Cu for conduction. The samples were then ground, starting with a coarse paper in order to remove surface defects, then finer and finer, ending with 1  $\mu$ m diamond paste polishing. Finally, the samples were cleaned thoroughly in ethanol in a ultrasonic bath. In order to treat the samples and the standard references (Appendices A and B) as equally as possible, both the samples and the standard references were polished 30 s with 1  $\mu$ m diamond paste and cleaned in ultrasonic bath, before each measurement occasion. Neither the samples nor the references were coated with a conductive layer.

### Phase composition analysis with EDS/WDS

The phase compositions were determined using a Hitachi S3700N scanning electron microscope equipped with a thermionic W filament and a Quantax EDS/WDS system (Fig. 2). Cr and Ti contents were measured with EDS and C contents with WDS. For both EDS and WDS measurements, a TiC standard (Appendix A) was used as reference for Ti and C, and a Cr<sub>3</sub>C<sub>2</sub> standard (Appendix B) was used as reference for Cr. Settings used were: working distance, 14.5 mm; acceleration voltage, 15 kV;  $\phi - \rho - Z$  correction. For WDS, a 80-Å multi-layer diffraction crystal was used and the optical alignment was made with minimum 10000 counts. Instead of direct measurements of the beam current, a system factor calibration was performed regularly on a piece of pure copper, mounted in the same resin as the sample, in order to compensate for the change in beam current. For each phase, five measurements were taken on two different occasions, in total ten measurements per phase, where all measured grains

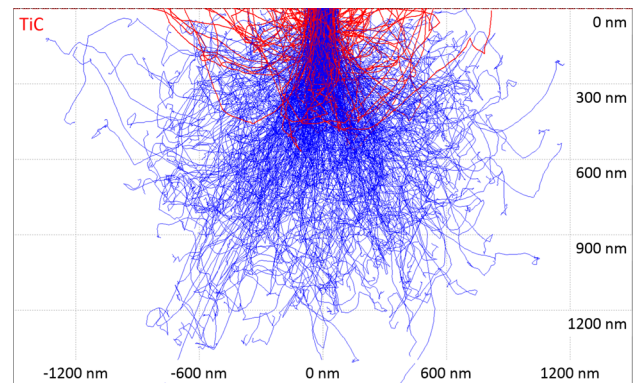


**Figure 2** Example of microstructures. MC– $M_3C_2$ – $M_7C_3$ , sample S21a (a) and MC– $M_3C_2$ –graphite, sample S22b (b).

were larger than  $3 \mu\text{m}$ . A Monte Carlo simulation of electron trajectories in solid TiC, assuming a beam diameter of 100 nm, using the software Casino v2.51, shows that this grain size should be sufficiently large as long as the depth of the grains are larger than  $1.5 \mu\text{m}$  (Fig. 3). Five measurements were taken on the standards before and after the measurements on the samples. The measurement closest to average, of these ten standard measurements, was used as reference at that specific occasion.

### XRD/Rietveld analysis

XRD measurements were taken with a Bruker D8 Discover equipped with a Cu- $K_\alpha$  X-ray tube ( $\lambda = 1.5418 \text{ \AA}$ ), a  $\phi 1.0$ -mm collimator and a LynxEye 1D-detector. 40 kV and 40 mA were used and the measurements were taken in the  $2\theta$  range  $10$ – $140^\circ$  with a step size of  $\Delta(2\theta) = 0.010^\circ$  and a scanning speed of  $5.0 \text{ s/step}$ .



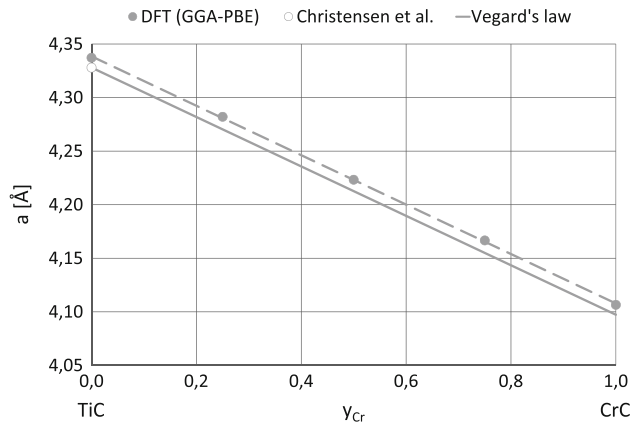
**Figure 3** Monte Carlo simulation of electron trajectories in solid TiC (red lines = backscattered electrons, blue lines = X-rays). Acceleration voltage = 15 kV, beam diameter = 100 nm.

The software PANalytical HighScore Plus 3.0d was then used for the Rietveld refinements [8]. Backgrounds were modelled with a Chebyshev polynomial of first kind and the peak profile shapes with the pseudo-Voigt function. The Cr-rich carbides ( $M_3C_2$  and  $M_7C_3$ ) were assumed to be pure Cr carbides with a stoichiometric C content. Structures from the studies by Christensen et al. [9] (TiC,  $Fm\bar{3}m$ ), Rundqvist et al. [10] ( $Cr_3C_2$ ,  $Pnma$ ), Rouault et al. [11] ( $Cr_7C_3$ ,  $Pnma$ ) and Fayos [12] (graphite,  $P6_3mc$ ) were used as starting structures for the refinement. The following parameters were refined: specimen displacement, scale factor, preferred orientation (not for graphite), lattice parameters (for graphite only c axis), Caglioti parameters (for graphite only U), peak shape 1 (not for graphite) and Asymmetry (only for graphite).

Refined lattice parameters for MC were then recalculated to compositions by using the experimental value of the lattice parameter for pure TiC [9], and assuming the lattice parameter changes according to Vegard's law [13] with a slope given by density functional theory (DFT) calculations [14] of the lattice parameters for pure TiC and pure CrC ( $Fm\bar{3}m$ ). Calculated lattice parameters of three disordered mixed carbides, ( $Ti_{0.75}Cr_{0.25}C$ ,  $Ti_{0.5}Cr_{0.5}C$  and  $Ti_{0.25}Cr_{0.75}C$ ) show that Vegard's law is a valid assumption in this case (Fig. 4).

### DFT calculations

The DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) [15] with projector augmented wave (PAW) potentials



**Figure 4** MC (M = Ti, Cr) lattice parameter,  $a$ , as a function of site fraction of Cr,  $y_{Cr}$ . TiC experimental lattice parameter by Christensen et al. [9].

[16] together with the Perdew–Burke–Ernzerhof (PBE) [17] version of the generalized gradient approximation (GGA). The equilibrium lattice parameters were found by calculating the energy ( $E$ ) for 7 different volumes ( $V$ ) and then fitting the Birch–Murnaghan equation of state [18, 19] to the  $E$ – $V$  curve. For the pure carbides (TiC and metastable CrC) a cell of 8 atoms, a  $k$ -point mesh of  $15 \times 15 \times 15$  and an energy cutoff of 750 eV were used, which corresponds to an energy convergence of  $< 1$  meV/atom. The energies of the mixed carbides were calculated using a  $2 \times 2 \times 2$  special quasirandom structure (SQS) supercell containing 64 atoms, with a  $k$ -point mesh of  $5 \times 5 \times 5$  and an energy cutoff of 750 eV, which again corresponds to an energy convergence of  $< 1$  meV/atom.

## Results

For each phase and equilibrium, 10 grains were analysed. Cr and Ti contents were analysed with EDS and C contents with WDS. A few outliers were rejected (4 of totally 200 measurements), and averages as well as standard deviations were calculated. The results were also validated with XRD measurements together with Rietveld refinement. As an example, Fig. 5 shows the measured diffraction pattern for sample S21b and the corresponding calculated pattern from the Rietveld refinement.

### Equilibrium MC– $M_3C_2$ – $M_7C_3$

For the equilibrium MC– $M_3C_2$ – $M_7C_3$ , the solubility of Cr in MC, at 1673 K was measured with EDS to  $5.30 \pm 0.61$  at.% and  $5.47 \pm 0.87$  at.% (S11a and S11b, Table 2). XRD measurements in combination with Rietveld refinement on the same samples are in rather good agreement with 4.33 at.% and 5.17 at.%, respectively (Table 3 and Fig. 6).

At 1773 K, the solubility of Cr in MC, for the same equilibrium, was measured to be  $7.83 \pm 1.30$  at.% and  $9.54 \pm 1.08$  at.% (S21a and S21b, Table 2). Here, the XRD measurements give a somewhat lower solubility, 6.53 at.% and 7.87 at.%, respectively (Table 3 and Fig. 6).

According to the WDS measurements the C content in MC, in this equilibrium, is close to, or just below 49 at.% (S11a, S11b, S21a and S21b, Table 2).

The present study also shows that the solubility of Ti in  $M_3C_2$  and in  $M_7C_3$  is around 2.0 at.% and 0.9 at.%, respectively, at both 1673 and 1773 K, in the MC– $M_3C_2$ – $M_7C_3$  equilibrium (S11a, S11b, S21a and S21b, Table 2).

### Equilibrium MC– $M_3C_2$ –graphite

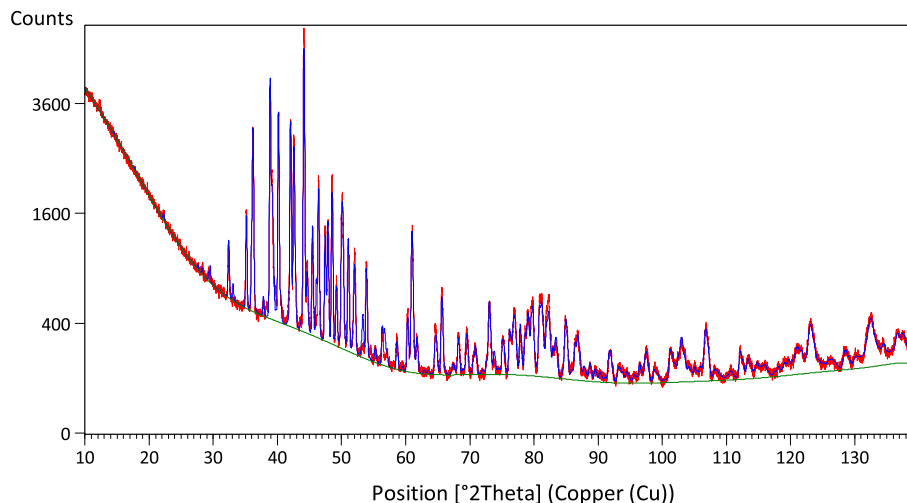
For the equilibrium MC– $M_3C_2$ –graphite, the solubility of Cr in MC, at 1673 K was measured with EDS to  $9.24 \pm 0.62$  at.% and  $9.34 \pm 1.01$  at.% (S12a and S12b, Table 4). XRD measurements in combination with Rietveld refinement on the same samples confirm these results with 8.82 at.% and 9.85 at.%, respectively (Table 5 and Fig. 7).

At 1773 K, the solubility of Cr in MC, for the same equilibrium, was measured with EDS to  $16.28 \pm 0.73$  at.% and  $18.61 \pm 0.33$  at.% (S22a and S22b, Table 4). Also here the XRD measurements are in good agreement, 16.24 at.% and 17.54 at.% Cr, respectively (S22a and S22b, Table 5 and Fig. 7).

For this equilibrium, the WDS measurements show that the C content in MC is close to or just above 49 at.% (S12a, S12b, S22a and S22b, Table 4).

Similar to the equilibrium MC– $M_3C_2$ – $M_7C_3$ , the solubility of Ti in  $M_3C_2$  in equilibrium MC– $M_3C_2$ –graphite is around 2.0 at.%, at both 1673 and 1773 K (S12a, S12b, S22a and S22b, Table 4).

**Figure 5** Sample S21b—  
Calculated diffraction pattern  
using the Rietveld refined  
phase structures (blue)  
compared with the measured  
diffraction pattern (red).



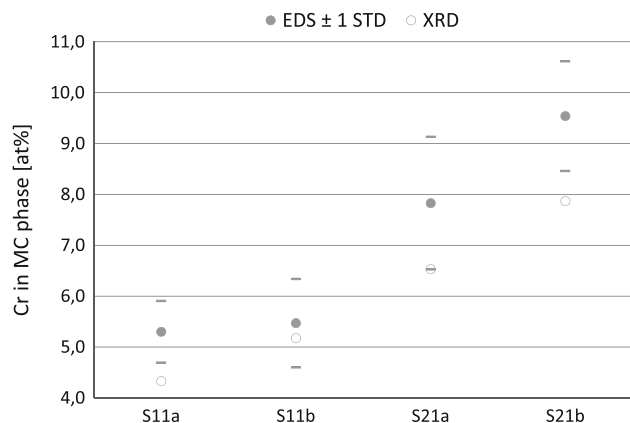
**Table 2** MC–M<sub>3</sub>C<sub>2</sub>–M<sub>7</sub>C<sub>3</sub>—  
Measured phase compositions  
±1 standard deviation, EDS/  
WDS

Temperature [K (°C)]	Phase	Sample	Ti (at.%)	Cr (at.%)	C (at.%)
1673 (1400)	MC	S11a	45.23 ± 0.81	5.30 ± 0.61	49.47 ± 0.44
		S11b	45.80 ± 1.10	5.47 ± 0.87	48.73 ± 0.64
	M <sub>3</sub> C <sub>2</sub>	S11a	1.73 ± 0.37	57.06 ± 0.41	41.21 ± 0.21
		S11b	1.97 ± 0.18	58.38 ± 0.57	39.66 ± 0.54
	M <sub>7</sub> C <sub>3</sub>	S11a	0.95 ± 0.08	68.77 ± 0.70	30.28 ± 0.68
		S11b	0.82 ± 0.21	69.27 ± 0.65	29.91 ± 0.75
1773 (1500)	MC	S21a	43.81 ± 1.55	7.83 ± 1.30	48.36 ± 0.88
		S21b	41.72 ± 1.42	9.54 ± 1.08	48.75 ± 0.62
	M <sub>3</sub> C <sub>2</sub>	S21a	1.98 ± 0.14	57.36 ± 0.82	40.66 ± 0.82
		S21b	2.06 ± 0.21	57.35 ± 0.48	40.60 ± 0.43
	M <sub>7</sub> C <sub>3</sub>	S21a	0.93 ± 0.07	68.37 ± 0.56	30.70 ± 0.58
		S21b	0.84 ± 0.11	68.51 ± 0.47	30.65 ± 0.54

**Table 3** MC–M<sub>3</sub>C<sub>2</sub>–M<sub>7</sub>C<sub>3</sub>—  
Rietveld refined lattice  
parameters (present work)  
compared with lattice  
parameters of pure TiC, Cr<sub>3</sub>C<sub>2</sub>  
and Cr<sub>7</sub>C<sub>3</sub> (literature)

Phase		1673 K		1773 K		Literature		
<i>Space group</i>		S11a	S11b	S21a	S21b			
MC	Lattice parameter	a (Å)	4.308	4.304	4.298	4.292	4.328 [9]	
	Composition*	Ti (at.%)	45.67	44.83	43.47	42.13		
		Cr (at.%)	4.33	5.17	6.53	7.87		
M <sub>3</sub> C <sub>2</sub>	Lattice parameter	a (Å)	5.533	5.532	5.533	5.532	5.533 [10]	
		b (Å)	2.839	2.840	2.841	2.841		2.829 [10]
		c (Å)	11.479	11.480	11.481	11.481		
	Cell volume	V (Å <sup>3</sup> )	180.330	180.389	180.488	180.475	179.565 [10]	
M <sub>7</sub> C <sub>3</sub>	Lattice parameter	a (Å)	4.525	4.523	4.524	4.524	4.526 [11]	
		b (Å)	7.019	7.018	7.017	7.019		7.010 [11]
		c (Å)	12.160	12.161	12.163	12.159		
	Cell volume	V (Å <sup>3</sup> )	386.179	386.025	386.069	386.046	385.23 [11]	
Refinement	Goodness of fit	GoF	4.59	7.95	9.45	3.73		

\*Composition calculated using Vegard’s law [13], C content assumed to be stoichiometric



**Figure 6** MC–M<sub>3</sub>C<sub>2</sub>–M<sub>7</sub>C<sub>3</sub> - Measured amount of Cr in MC: EDS compared with XRD/Rietveld.

## Discussion

The objective of the experiments in this work was to study the equilibria MC–M<sub>3</sub>C<sub>2</sub>–M<sub>7</sub>C<sub>3</sub> (M = Ti, Cr) and MC–M<sub>3</sub>C<sub>2</sub>–graphite in the Ti–Cr–C system. The main purpose was to determine the solubility of Cr in MC, but the solubility of Ti in M<sub>3</sub>C<sub>2</sub> and M<sub>7</sub>C<sub>3</sub> was also of interest, as well as the C content in MC.

For the MC–M<sub>3</sub>C<sub>2</sub>–M<sub>7</sub>C<sub>3</sub> equilibrium (Fig. 8a), the solubility of Cr in MC (M = Ti, Cr), measured with EDS in this work (5.30–5.47 at.% at 1673 K and 7.83–9.54 at.% at 1773 K) is much lower than the solubilities calculated with the thermodynamic description by Schuster et al. [6] and the solubility at 1773 K (20.7 at.%) reported by Booker et al. [1]. This difference is also significant for the MC–M<sub>3</sub>C<sub>2</sub>–graphite equilibrium (Fig. 8b), especially at 1673 K where the

**Table 4** MC–M<sub>3</sub>C<sub>2</sub>–graphite—Measured phase compositions ±1 standard deviation, EDS/WDS

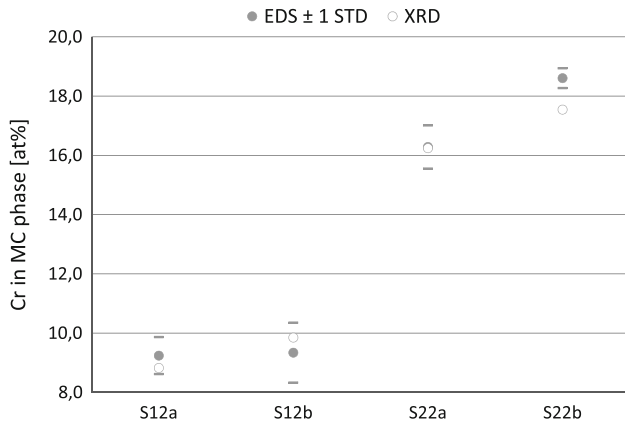
Temperature [K (°C)]	Phase	Sample	Ti (at.%)	Cr (at.%)	C (at.%)
1673 (1400)	MC	S12a	41.96 ± 1.04	9.24 ± 0.62	48.81 ± 0.60
		S12b	41.19 ± 0.85	9.34 ± 1.01	49.47 ± 0.67
	M <sub>3</sub> C <sub>2</sub>	S12a	1.86 ± 0.45	57.38 ± 0.83	40.76 ± 1.01
		S12b	1.98 ± 0.20	57.42 ± 0.39	40.61 ± 0.50
1773 (1500)	MC	S22a	34.51 ± 1.40	16.28 ± 0.73	49.21 ± 1.02
		S22b	32.05 ± 0.65	18.61 ± 0.33	49.35 ± 0.53
	M <sub>3</sub> C <sub>2</sub>	S22a	2.01 ± 0.31	56.63 ± 0.53	41.36 ± 0.57
		S22b	2.02 ± 0.15	57.66 ± 0.65	40.32 ± 0.67

**Table 5** MC–M<sub>3</sub>C<sub>2</sub>–graphite—Rietveld refined lattice parameters (present work) compared with lattice parameters of pure TiC, Cr<sub>3</sub>C<sub>2</sub> and graphite (literature)

Phase	1673 K		1773 K		Literature		
	S12a	S12b	S22a	S22b			
MC	Lattice parameter	a (Å)	4.287	4.283	4.253	4.247	4.328 [9]
<i>Fm</i> $\bar{3}$ <i>m</i>	Composition*	Ti (at.%)	41.18	40.15	33.76	32.46	
		Cr (at.%)	8.82	9.85	16.24	17.54	
M <sub>3</sub> C <sub>2</sub>	Lattice parameter	a (Å)	5.530	5.531	5.532	5.532	5.533 [10]
<i>Pnma</i>		b (Å)	2.836	2.839	2.837	2.841	
		c (Å)	11.479	11.482	11.485	11.479	11.472 [10]
	Cell volume	V (Å <sup>3</sup> )	180.017	180.301	180.233	180.388	179.565 [10]
Graphite	Lattice parameter**	a (Å)	2.461	2.461	2.461	2.461	2.461 [12]
<i>P6</i> <sub>3</sub> <i>mc</i>		b (Å)	2.461	2.461	2.461	2.461	
		c (Å)	6.724	6.713	6.722	6.710	6.708 [12]
	Cell volume	V (Å <sup>3</sup> )	40.723	40.658	40.713	40.641	40.627 [12]
Refinement	Goodness of fit	GoF	9.18	1.70	13.44	2.55	

\*Composition calculated using Vegard's law [13], C content assumed to be stoichiometric

\*\*Lattice parameter *a* and *b* for graphite not refined



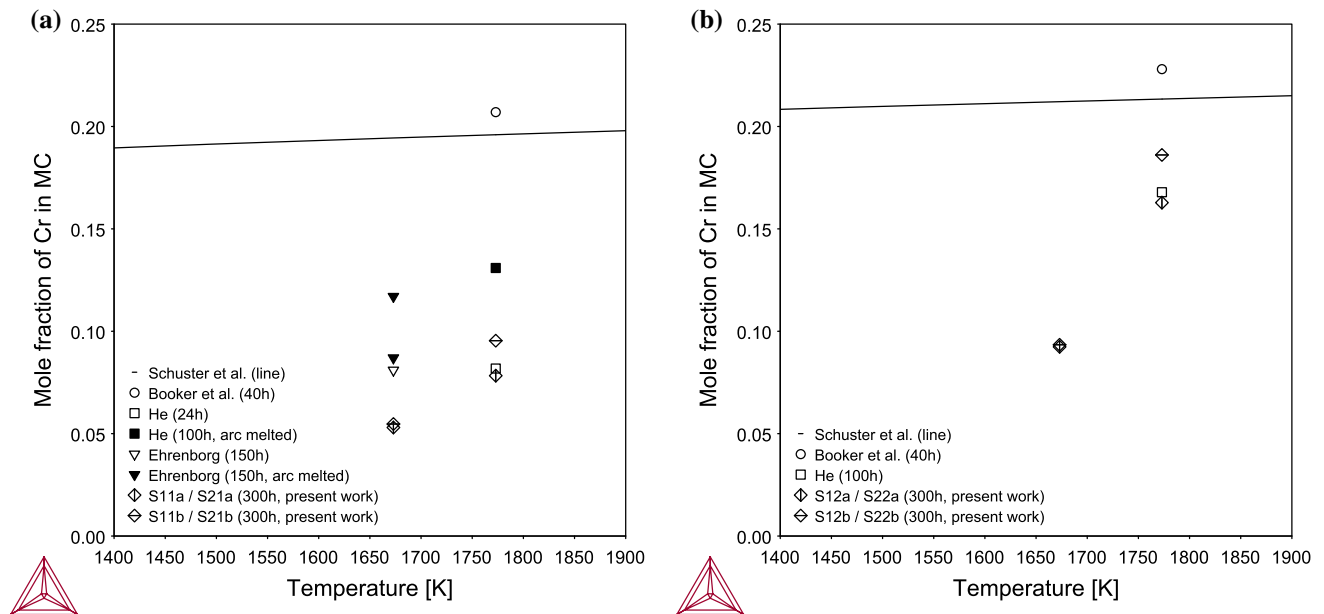
**Figure 7** MC–M<sub>3</sub>C<sub>2</sub>–graphite—Measured amount of Cr in MC: EDS compared with XRD/Rietveld.

measurements in the present work show a solubility of Cr in MC of 9.24–9.34 at.% and the solubility calculated with the thermodynamic description by Schuster et al. [6] is above 20 at.%. At 1773 K, the difference is less prominent, but still clear, 16.28–18.61 at.% (present work) compared to 22.8 at.% reported by Booker et al. [1].

The results from this study are in somewhat better agreement with the findings by Ehrenborg [3] and He [2], even if they also report larger solubilities of Cr in MC. What is clear though is that their results show that samples that are arc-melted prior to the equilibration heat treatment give a higher solubility than

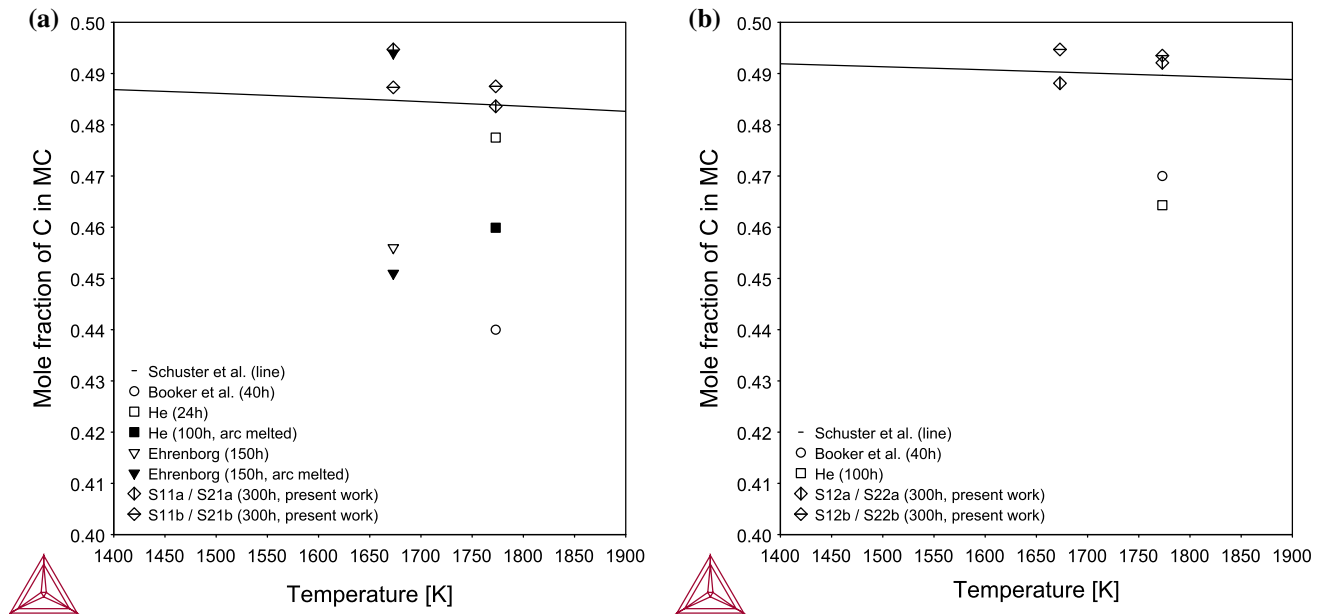
non-arc-melted ones. Since the solubility of Cr in MC increases with the temperature, arc-melted samples will start the equilibration process with a too high Cr content in MC. If the equilibration time then is too short, the solubility will be overestimated. For non-arc-melted samples, on the other hand, it will be the opposite, i.e. a too short heat treatment time may lead to an underestimated solubility because the solubility is lower at lower temperatures. Also, arc-melted samples faced a higher temperature than non-arc-melted ones, and thus, they will also have larger grains, meaning the diffusion paths will be longer and the time needed to reach equilibrium will increase further. As Fig. 8 also shows, all arc-melted samples yield a higher solubility of Cr in MC than the non-arc-melted ones, except for the sample by Booker et al. [1]. However, the samples used in the experiments by Booker et al. [1] were not arc-melted, but hot pressed at 2173 K (Booker et al. used the same method as reported by Rudy et al. [20]), i.e. significantly higher than the equilibration temperature. In other words, with insufficient equilibration time, these samples will also overestimate the solubility.

In general, the a- and b-samples in this work are in good agreement with each other, indicating that the used equilibration time of 300 h is sufficient. There are some deviations however, which could arise from differences in the used raw materials, e.g. Cr has been



**Figure 8** Measured solubility of Cr in MC compared with literature for the MC–M<sub>3</sub>C<sub>2</sub>–M<sub>7</sub>C<sub>3</sub> equilibrium (a) and the MC–M<sub>3</sub>C<sub>2</sub>–graphite equilibrium (b). Equilibration times within parenthesis.





**Figure 9** Measured C content in MC compared with literature for the MC-M<sub>3</sub>C<sub>2</sub>-M<sub>7</sub>C<sub>3</sub> equilibrium (a) and the MC-M<sub>3</sub>C<sub>2</sub>-graphite equilibrium (b). Equilibration times within parenthesis.

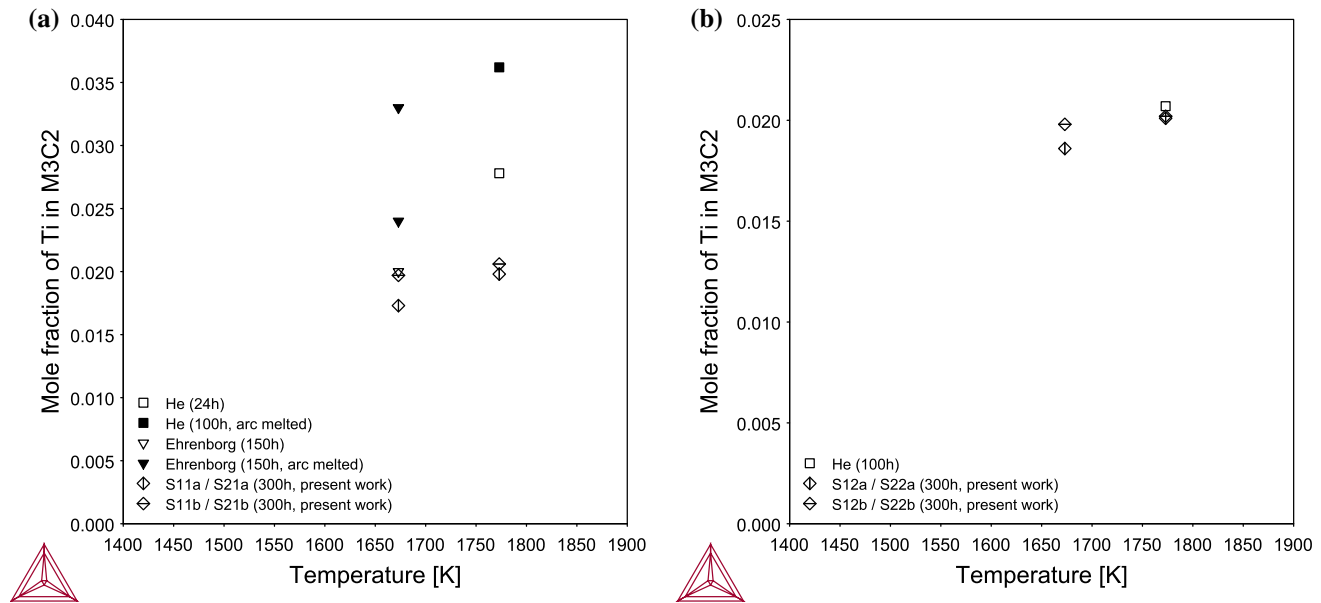
used for a-samples, while Cr<sub>7</sub>C<sub>3</sub> was used for the b-samples (Table 1). One reason for the different results could therefore be the rather high amount of O (0.8 wt%) in the Cr raw material. Even if extra carbon black was added in order to compensate for oxide reduction during the processing, this could have given other effects, e.g. as more porosity in the heat-treated samples. Additionally, there is also a risk that all oxides were not reduced, which in that case directly would affect the equilibrium phase compositions. However, as only expected phases were included in the Rietveld refinement any O containing phase, or other type of contamination, would have given diffraction peaks not possible to fit, resulting in a increased goodness-of-fit (GoF) value. As Tables 3 and 5 show, the GoF is also, in general, better for the b-samples and especially for the samples in equilibrium MC-M<sub>3</sub>C<sub>2</sub>-graphite, which indicates that the b-samples in this study are more reliable.

Another source of error is the actual temperature used for the experiments. For example, the experiments in this study show that the solubility of Cr in MC increases by about 9 at.%, when the temperature is increased from 1673 to 1773 K (Table 4 and Fig. 8b), i.e. even a small temperature error gives rise to a rather large change in measured composition and a carefully controlled temperature is thus important.

To assure this, the furnace temperature was controlled with PTCRs and samples of pure Ni as described in “Sample synthesis” section.

The fact that the XRD measurements in combination with Rietveld refinement are in good agreement with the EDS measurements (Figs. 6 and 7) shows that the EDS measurements are reliable. There are some deviations though, especially for the MC-M<sub>3</sub>C<sub>2</sub>-M<sub>7</sub>C<sub>3</sub> equilibrium, where the XRD/Rietveld refinement gives a somewhat lower Cr solubility in MC. This could to some extent be explained by the fact that for the XRD/Rietveld refinement case, the Cr content in MC has been calculated by assuming that MC is stoichiometric. As Tables 2 and 4 show, the C content in MC is, in fact, sub-stoichiometric, and especially for the MC-M<sub>3</sub>C<sub>2</sub>-M<sub>7</sub>C<sub>3</sub> equilibrium, and hence, this assumption will underestimate the Cr content.

The C contents in MC, measured with WDS in this work are higher than previously reported by Booker et al. [1], He [2] and Ehrenborg [3] (except for one sample by Ehrenborg [3]), for both the MC-M<sub>3</sub>C<sub>2</sub>-M<sub>7</sub>C<sub>3</sub> equilibrium (Fig. 9a) and the MC-M<sub>3</sub>C<sub>2</sub>-graphite equilibrium (Fig. 9b). These rather big differences in measured C content could be a result of whether thermodynamic equilibrium has been reached or not, but the differences could also be a



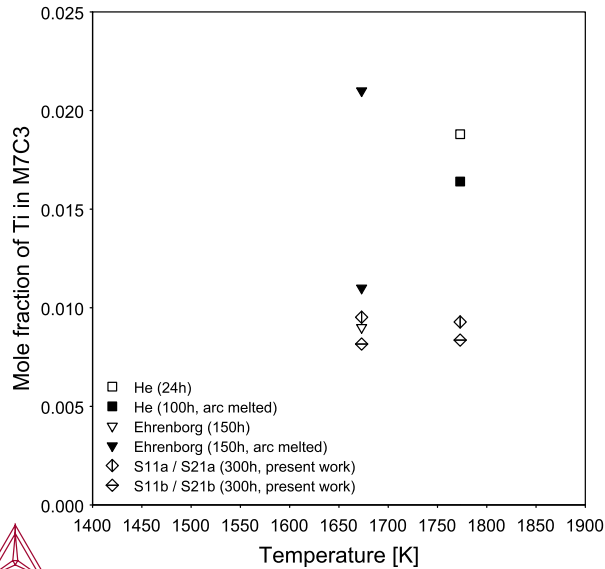
**Figure 10** Measured Ti content in  $M_3C_2$  compared with literature for the MC- $M_3C_2$ - $M_7C_3$  equilibrium (a) and the MC- $M_3C_2$ -graphite equilibrium (b).

result of inaccuracy in the analysis of the samples. Reasons for inaccuracy could, for example, be that porosity causes contamination from the sample preparation; that the electron beam induces C deposition on the sample; use of conductive layer on the sample, on the standard reference, or both; or that the used standard reference is not ideal.

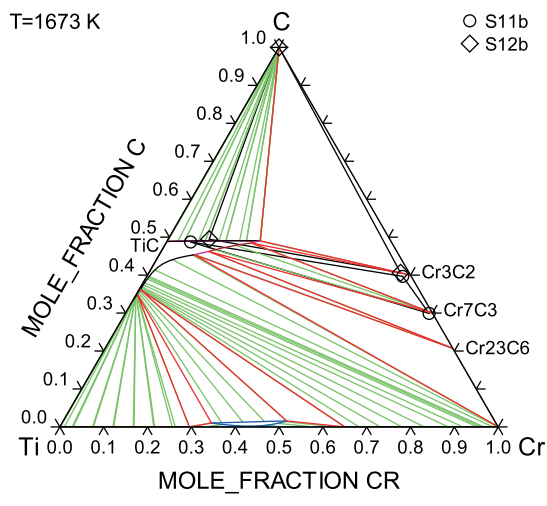
On the other hand, the C contents in MC, measured in this work, are in surprisingly good agreement with the thermodynamic description by Schuster et al. [6], for both the MC- $M_3C_2$ - $M_7C_3$  equilibrium (Fig. 9a) and the MC- $M_3C_2$ -graphite equilibrium (Fig. 9b). Schuster et al. [6] mainly based their assessment of the Ti-Cr-C system on the findings by Booker et al. [1], but also, for example, on the findings by Kerans et al. [21]. Kerans et al. [21] found the maximum C content in MC, at 2273 K, to be 49 at.%. In order to fit a thermodynamic model to the C content in MC measured by Booker et al. [1], the reciprocal interaction parameter ( $L_{Cr,Ti,C,Va}^{FCC}$ ) has to be used. Schuster et al. [6] have not used this parameter, which indicates that they relied more on the findings by Kerans et al. [21]. The results from this work, for the MC- $M_3C_2$ -graphite equilibrium, show that the C content in MC is just above 49 at.% (Fig. 9b), at both 1673 and 1773 K, which also are in line with the findings by Kerans et al. [21].

The solubilities of Ti in  $M_3C_2$  and  $M_7C_3$ , in the MC- $M_3C_2$ - $M_7C_3$  equilibrium, measured with EDS in this work are in good agreement with the results of the non-arc-melted sample by Ehrenborg [3] at 1673 K, while they are a bit lower than the findings by He [2] at 1773 K (Figs. 10a and 11); however, the sample by He [2] was only heat-treated for 24 h. For the MC- $M_3C_2$ -graphite equilibrium, on the other hand, the agreement with the non-arc-melted sample by He [2] is very good at 1773 K (Fig. 10b). This sample by He [2] was heat-treated for 100 h, which indicates that 24 h is an insufficient equilibration time. Booker et al. [1] did not explicitly give the solubility of Ti in the Cr carbides, but from their published isothermal sections it can be estimated to be low and Schuster et al. [6] have not modelled these solubilities.

In general, the results in the present study are aligned with previous results from the literature. Differences in solubility of Cr in MC can be explained by the differences in heat treatment time or whether the sample was arc-melted or not. Also, differences in the Ti content in  $M_3C_2$  and  $M_7C_3$  can be explained in the same way. The scattered results of C content in MC, in this work compared with literature, are, on the other hand, not easily explained, and further studies might be needed in order to confirm these results.

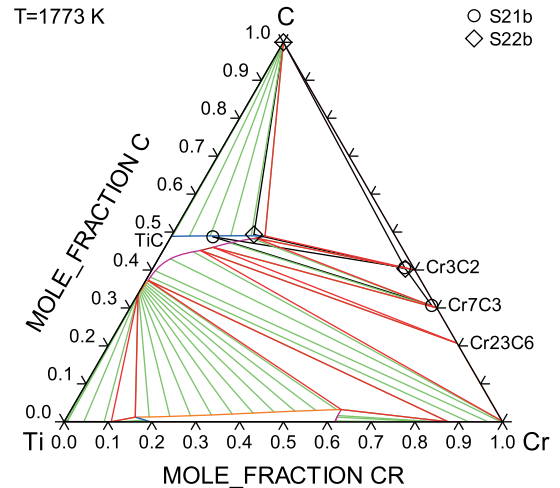


**Figure 11** Measured Ti content in  $M_7C_3$  compared with literature for the  $MC-M_3C_2-M_7C_3$  equilibrium.



**Figure 12** Ti–Cr–C isothermal section according to the description by Schuster et al. [6] at 1673 K. Markers show measured phase compositions of b-samples in this work.

In summary, the long heat treatment time (300 h), the use of non-arc-melted samples, the fact that the a- and b-samples give rather equal results and the careful temperature calibration and sample preparation, the results of the b-samples in this study should be close to thermodynamic equilibrium.



**Figure 13** Ti–Cr–C isothermal section according to the description by Schuster et al. [6] at 1773 K. Markers show measured phase compositions of b-samples in this work.

## Conclusions

The objective of this work was to study the equilibria  $MC-M_3C_2-M_7C_3$  ( $M = Ti, Cr$ ) and  $MC-M_3C_2$ -graphite in the Ti–Cr–C system in order to determine the equilibrium phase compositions. Experiments were performed at 1673 and 1773 K with a heat treatment time of 300 h. The main purpose was to determine the solubility of Cr in MC, but the solubility of Ti in  $M_3C_2$  and  $M_7C_3$  was also of interest, as well as the C content in MC. Another important issue was to verify that the used heat treatment time was sufficient in order to reach equilibria.

The conclusions are that with the current conditions a heat treatment time of 300 h is sufficient in order to reach thermodynamic equilibrium. This study shows that the solubility of Cr in MC ( $M = Ti, Cr$ ) was overestimated by Booker et al. [1], and by the thermodynamic description of the Ti–Cr–C system by Schuster et al. [6] since they mainly based their assessment of the Ti–Cr–C system on the findings by Booker et al. [1] (see Fig. 8). The overestimated solubility by Booker et al. [1] was probably due to sample synthesis at a temperature higher than the heat treatment temperature in combination with an insufficient heat treatment time. This study also shows that the Cr solubility in MC rapidly increases with temperature, especially for the  $MC-M_3C_2$ -graphite equilibrium (see S11b/S21b in Table 2 and S12b/S22b in Table 4).

The C contents in MC, measured in this study, are higher than those reported by Booker et al. [1], He [2] and Ehrenborg [3], but are nevertheless in surprisingly good agreement with the thermodynamic description of the Ti–Cr–C system by Schuster et al. [6] (see Fig. 9, S11b/S21b in Table 2 and S12b/S22b in Table 4).

Further, this study also shows that there is a solubility of Ti both in  $M_3C_2$  and in  $M_7C_3$  (see S11b/S21b in Table 2 and S12b/S22b in Table 4), but in the thermodynamic description by Schuster et al. [6] these solubilities have not been modelled.

Figures 12 and 13 show isothermal sections of the Ti–Cr–C system, at 1673 and 1773 K, respectively, calculated using the Thermo-Calc Software [5] with the thermodynamic description of the Ti–Cr–C system by Schuster et al. [6]. Markers in the figures show measured phase compositions of b-samples in this work (see S11b/S21b in Table 2 and S12b/S22b in Table 4) and illustrate how the thermodynamic description by Schuster et al. [6] should be updated in order to fit the results of this work.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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