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## PHASE DIAGRAM OF THE Ti-V-C SYSTEM AT 1000 AND 1200° C

### WYKRES FAZOWY UKŁADU Ti-V-C W TEMPERATURZE 1000 ORAZ 1200° C

The ternary Ti-V-C system was studied experimentally at 1000 and 1200°C. Phase diagram data for this system and relevant subsystems has been collected and theoretical assessment was carried out. New thermodynamic parameters in Hillert-Staffansson model were assessed. Experimental results, both own and taken from literature were compared with calculated phase diagrams in order to support and verify suggested data. Reasonable agreement was obtained between the calculation and the experiments.

Zbadano doświadczalnie układ Ti-V-C w temperaturach 1000 oraz 1200°C. Zebrano i krytycznie opracowano dane dotyczące tego układu oraz składowych układów podwójnych. Określono parametry termodynamiczne w modelu Hillerta-Staffanssona. W celu weryfikacji danych porównano obliczony wykres fazowy z rezultatami badań własnych i z literatury. Stwierdzono dobrą zgodność pomiędzy rezultatami z obliczeń oraz z badań.

### 1. Introduction

Titanium and vanadium carbides form hard and resistant materials, which are widely used in the industry for tools and water-resistant applications and even as fuel cladding in the nuclear power plants. Despite of their importance, only few experiments, dealing with the phase diagrams of Ti-V-C systems, were made, most of them in the second half of the 60's. The system was studied in the temperature range 1000°C — melting point ( $\sim 2700^\circ\text{C}$ ). Eremenko [1] and Tret'yachenko [2, 3] constructed isothermal sections at 1450, 1600

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and 1800°C. Fedrov [4] published isothermal section at 1000°C, concentration dependence of the lattice parameter for (Ti,V)C carbide and lattice parameter of V<sub>2</sub>C phase. Rudy [5] examined phase relationships in the Ti-V-C system by X-ray diffraction in the temperature range 1400–2700°C.

(βTi) and (V) compose the BCC solid solution with unlimited mutual solubility; the solubility of carbon in the BCC phase is very small. B1 carbidic phases TiC and VC (denoted as δ) are also fully soluble. Another phase existing in this temperature region is the HCP γ-V<sub>2</sub>C. Rudy has found titanium solubility to be approx. 15 at % in this phase. No ternary phases were found.

Rudy constructed several isopleths at a few carbon concentrations. Tret'yachenko reported several solid isotherms in the whole composition range; Rudy also studied isotherms between 36 and 50 at %C. Experimental isothermal sections in the 1000–2700°C range show unusual change of δ phase field with the temperature. It does not increase monotonously with decreasing temperature between 1000–1200°C. Recent Ti-V-C review was published by Enomoto [6]. Theoretical studies and thermodynamic assessments for the Ti-V-C system do not exist.

## 2. Theoretical part

Hillert-Staffanssons sublattice model [7] and minimization of overall Gibbs energy were employed for the phase equilibria evaluations. Thermo-Calc [8] software package was used for calculations. Solid phases were modeled by two sublattices — (Ti, V)<sub>x</sub> : (C, Va)<sub>y</sub> with x : y ratios: FCC (δ) — 1 : 1, BCC (β) — 1 : 3, HCP (γ) — 1 : 0.5.

Expression for molar Gibbs energy of the solid phase *f* is

$$\begin{aligned}
 G^f = & y_{\text{Ti}}y_{\text{C}} {}^0G_{\text{Ti:C}}^f + y_{\text{Ti}}y_{\text{Va}} {}^0G_{\text{Ti:Va}}^f + y_{\text{V}}y_{\text{C}} {}^0G_{\text{V:C}}^f + y_{\text{V}}y_{\text{Va}} {}^0G_{\text{V:Va}}^f + \\
 & + RT \left[ (y_{\text{Ti}} \ln y_{\text{Ti}} + y_{\text{V}} \ln y_{\text{V}}) + b(y_{\text{C}} \ln y_{\text{C}} + y_{\text{Va}} \ln y_{\text{Va}}) \right] + \\
 & + y_{\text{Ti}}y_{\text{V}} \left( y_{\text{C}}L_{\text{Ti,V:C}}^f + y_{\text{Va}}L_{\text{Ti,V:Va}}^f \right) + y_{\text{C}}y_{\text{Va}} \left( y_{\text{Ti}}L_{\text{Ti:C,Va}}^f + y_{\text{V}}L_{\text{V:C,Va}}^f \right) + \\
 & + y_{\text{Ti}}y_{\text{V}}y_{\text{C}}y_{\text{Va}}L_{\text{Ti,V:C,Va}}^f
 \end{aligned} \quad (1)$$

*b* is 1 for FCC, 3 for BCC, 0.5 for HCP.

$G^f$  is molar Gibbs energy of the phase;  ${}^0G_{i:j}^f$  is molar Gibbs energy of hypothetical species *i* : *j*; *T* is absolute temperature; *R* is universal gas constant; *y* is site fraction; : separates sublattices; *L* is interaction parameter.

Liquid phase is modeled as one lattice substitutional solution. Expression for molar Gibbs energy of the liquid phase *l* is

$$\begin{aligned}
 G^l = & x_{\text{Ti}} {}^0G_{\text{Ti}}^l + x_{\text{V}} {}^0G_{\text{V}}^l + x_{\text{C}} {}^0G_{\text{C}}^l + RT(x_{\text{Ti}} \ln x_{\text{Ti}} + x_{\text{V}} \ln x_{\text{V}} + x_{\text{C}} \ln x_{\text{C}}) \\
 & + x_{\text{Ti}}x_{\text{V}}L_{\text{Ti,V}}^l + x_{\text{Ti}}x_{\text{C}}L_{\text{Ti,C}}^l + x_{\text{V}}x_{\text{C}}L_{\text{V,C}}^l + x_{\text{Ti}}x_{\text{V}}x_{\text{C}}L_{\text{Ti,V,C}}^l.
 \end{aligned} \quad (2)$$

In both expressions (1), (2) the terms with  ${}^0G$  form the reference surface of molar Gibbs energy (interactions between species on the neighbouring sublattices), the term with  $RT$  is ideal Gibbs energy of mixing. The next terms (with  $L$  parameters) are excess Gibbs energies, describing the interactions among species on the same sublattice.  $G$  and  $L$  parameters can be temperature and composition dependent; the temperature dependence is polynomial:

$${}^mL = {}^mA + {}^mB.T + {}^mC.T.\ln(T), \quad m = 0, 1, 2. \quad (3)$$

The composition dependence is given by Redlich-Kister formula:

$$L_{i,j;k} = {}^0L + {}^1L(x_i - x_j) + {}^2L(x_i - x_j)^2 + \dots \quad (4)$$

For calculations were used data for pure substances (Dinsdale [9]) and for binary subsystems: Ti-V (Kumar [10]), V-C (Huang [11]), Ti-C (Dumitrescu [12]).

### 3. Experimental Part

Experiments were carried out with alloys at normal pressure and temperatures 1000 and 1200°C. Five samples were prepared (nominal compositions in wt. %; specimen names in parenthesis): Ti-5V-5C (C1, D1), Ti-25V-5C (C2), Ti-25V-12C (C3, D2), Ti-70V-5C (C4) and Ti-70V-12C (C5, D3). The compositions were chosen with respect to the preliminary isothermal sections of the Ti-V-C phase diagram, calculated only from unary and binary data. Main attention was given to the extent of expected three-phase region. Experimental phase diagram for 1200°C not available in literature, the diagram for 1000°C was published by Fedrov [4].

$D^*$  specimens were annealed at the temperature 1000°C for 10 and 20 days,  $C^*$  specimens were annealed at 1200°C for 3 and 7 days. Kinetic studies showed that the structure of alloys treated for longer time is close to equilibrium state, because there is only minor change in phase composition in comparison with specimens after shorter annealing time. Specimens D3 and C5 contained three-phase structure (HCP + BCC + FCC), the only phases present in the other specimens were BCC and FCC. The detailed description of the experimental procedure will be described elsewhere [13].

### 4. Results and Discussion

Experimental results in the form of tie-lines (bold solid line) are compared with theoretical ones (dotted lines) in phase diagrams (Figs. 1 and 2). Calculated phase boundaries are drawn in thin solid lines. The content of carbon for the BCC phase was very low for reliable experimental measurements. Therefore, calculated

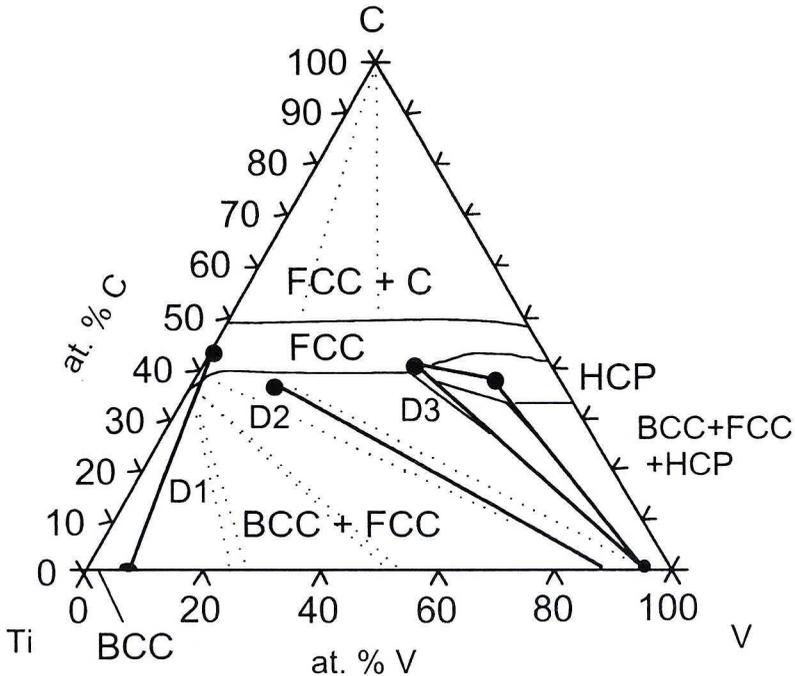


Fig. 1. Experimental ( $\bullet$ , bold solid lines) and calculated (dotted lines) tie-lines in the isothermal section of Ti-V-C phase diagram at 1000°C (thin solid lines) [calculated by Thermo-Calc]. Symbol  $\times$  represents the overall composition (measured by chemical analysis)

values of  $C$  content were used for the BCC phase of most specimens to complete measured compositions. Nevertheless, in some cases unusually high values of  $C$  in this phase were found experimentally. This can be explained by influence of surrounding carbides in the case where the BCC phase was sparse, and also by presence of very fine carbide particles, which were found in the BCC matrix.

The calculations with unary and binary data showed significant discrepancy in comparison with experiments (both Fedrov's and ours), especially in the area of three phase region FCC + BCC + HCP (i.e.  $(Ti, V)C + BCC + (V, Ti)_2C$ ) which was much larger than the experimental one. Hence we have proposed six interaction parameters  $L$ : two for HCP phase, three for FCC phase, one for liquid (Table) to obtain better fit between calculated and experimental phase diagrams.

Introduced interaction parameters led to very reasonable agreement between the calculations and experiments. Main difference is in the size of the FCC phase field, which should be narrower in the calculated diagram. Up to now, the authors were not successful in assessing of such parameters, which would give desirable results without unacceptable influence on the other phase fields in the diagram.

Our experimental results at 1000°C are similar to Fedrov's work. The carbon content in the FCC phase was for all specimens generally higher than tems from

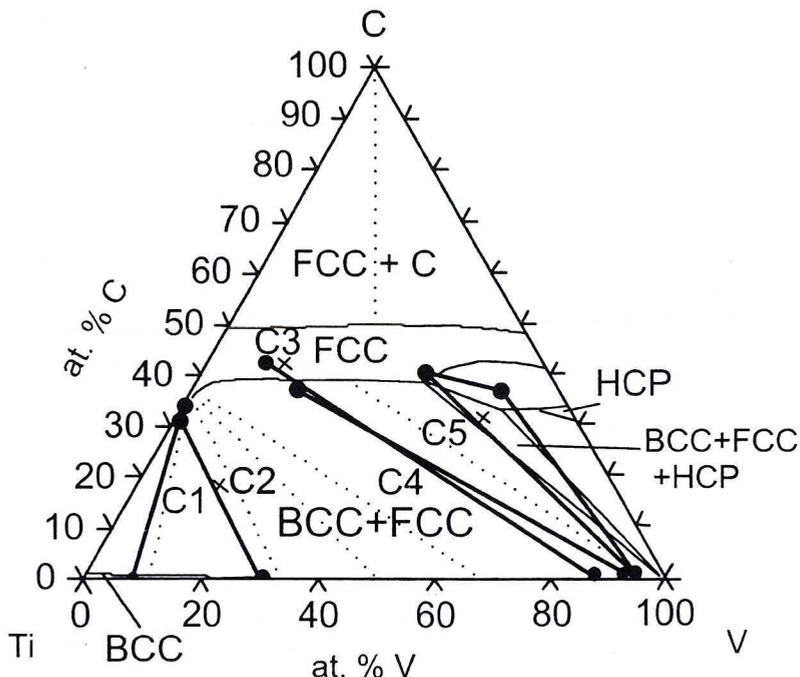


Fig. 2. Experimental (•, bold solid lines) and calculated (dotted lines) tie-lines in the isothermal section of Ti-V-C phase diagram at 1200°C (thin solid lines) [calculated by Thermo-Calc]. Symbol × represents the overall composition (measured by chemical analysis)

TABLE  
Proposed ternary interaction parameters for the  
Ti-V-C system

Parameter	Phase	Value [kJ/mol]
${}^0L_{Ti,V,C}$	HCP	$-26565 + 5 * T$
${}^0L_{Ti,V,C,Va}$	HCP	63300
${}^0L_{Ti,V,C}$	FCC	$-73912.5 + 12.5 * T$
${}^1L_{Ti,V,C}$	FCC	$97042.8 - 42.85 * T$
${}^0L_{Ti,V,C,Va}$	FCC	102000
${}^0L_{Ti,V,C}$	Liquid	24600

the calculations (see previous paragraph). It can be explained by relatively greater margin of error in the evaluation method for carbon, which was measured by the WDX in SEM [13]. The D3 sample had three-phase structure. Carbon content in the BCC phase had to be calculated because the measurement gave much higher *C* concentrations than expected for the BCC phase. Possible reasons were mentioned above. The overall composition of D3 sample lies very close to FCC + BCC side of three-phase area and hence it should contain only trace amount of

the HCP phase. Despite of this, significant amount of the HCP phase was found in the structure. This discrepancy can be explained by greater margin of error in the measurement of C contents in relevant phases (WDX method) in comparison with overall C content which was obtained by chemical analysis.

The experiments at 1200°C are in better agreement with calculated results than experiments at 1000°C. Unlike D1 sample, the FCC phase composition of C1 sample is very close to the calculated one. C5 sample had three-phase structure and the FCC and HCP apices of the triangle lie at higher carbon composition than the calculated ones. Again the only greater discrepancy between the calculation and experiments is in the carbon composition of the FCC phase.

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