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Thermodynamic and kinetic databases of cemented carbides and their applications to phase field simulation of microstructure during sintering

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1. Background

2. Thermodynamic and kinetic databases for cemented carbides

    2.1 Thermodynamic database

    2.2 Diffusion database

3. Simulation of microstructure in cemented carbides

    3.1 1D simulation of gradient cemented carbide

    3.2 1D and 2D simulations of cellular cemented carbide

4. Summary

1. Background

Cemented carbides is widely used in industry

Cutting Tools

Milling cutter

- Mold machining

Turning insert

- Stainless steel machining

Mechanical drills

Exploration drill

- Oilfield drilling, mining drilling

TBM

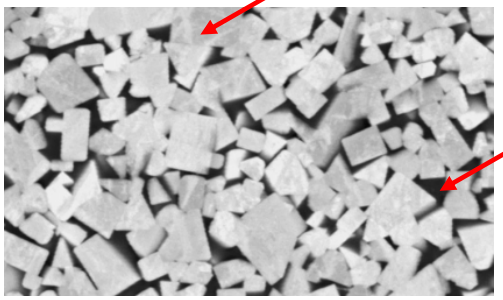
- Tunnel boring machine

1. Background

Two types of cemented carbides: tadeoff between toughness and hardness

Homogeneous Cemented Carbides

WC (hardness)



Binder (toughness)

WC grain size:

Extra coarse cemented carbide
Ultra fine cemented carbide

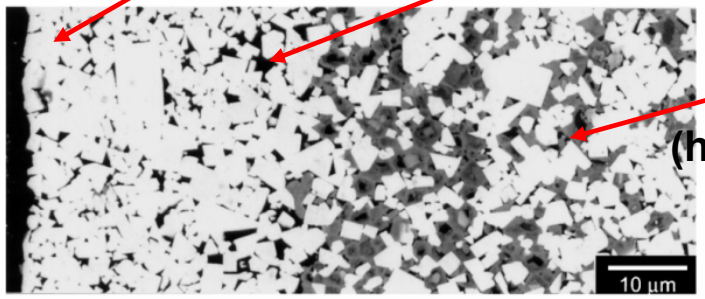
Binder:

Metal: Co, Ni, Fe
Intermetallics: Ni_3Al, FeAl…..

Gradient Cemented Carbides

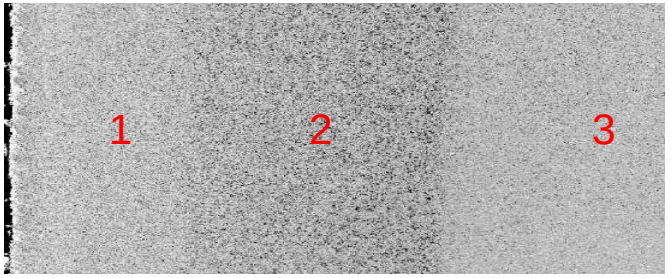
- **Nitrogen atmosphere sintering**

WC (hard phase) Binder (soft phase)



Cubic (hard phase)

- **C-controlling cemented carbide**



1:WC+Co(poor) **3:WC+Co(rich)+η**

2:WC+Co(rich)

1. Background

Challenges for design of multi-component cemented carbides

- more than 5 elements, sintering temp. & time, atmosphere etc
- Thermodynamic databases: unavailable or incomplete; No complete diffusion database
  - SANDVIK: C-Co-W-Ta-Ti-Nb-N (2001) 🕐 Commercially unavailable
  - Thermocalc: C-Co-W-Ta-Ti-Nb 🕐 Limited elements

Strategy for the production of new cemented carbides

Computational tools

CALPHAD+Experiment

Thermodynamic database

finished

First-principles calculation

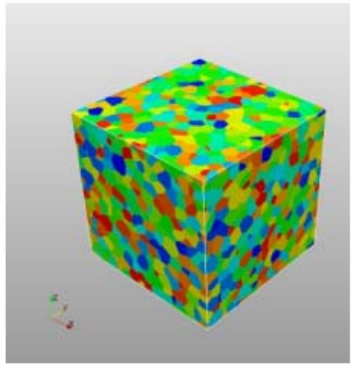
Interface energy
Elastice energy
….

In progress

CALPHAD+Experiment

Diffusion Database

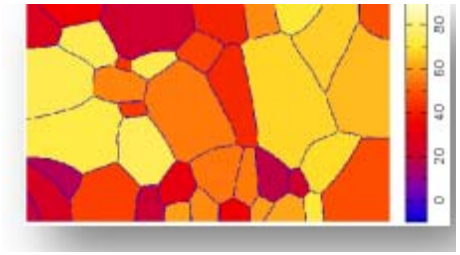
finished

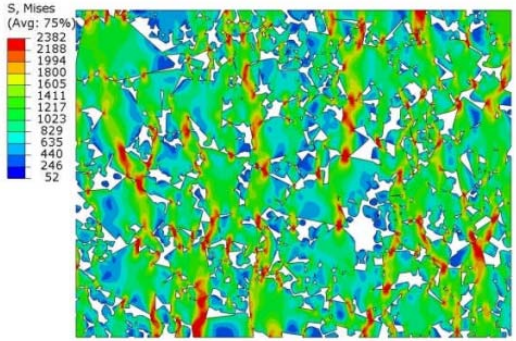


Phase field

Microstructure

In progress





Finite Element Analysis

Experimental methods

Hardness,
Fracture, toughness

In progress

Content

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2.1 Thermodynamic database

2.2 Diffusion database

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3.1 1D simulation of Gradient cemented carbide

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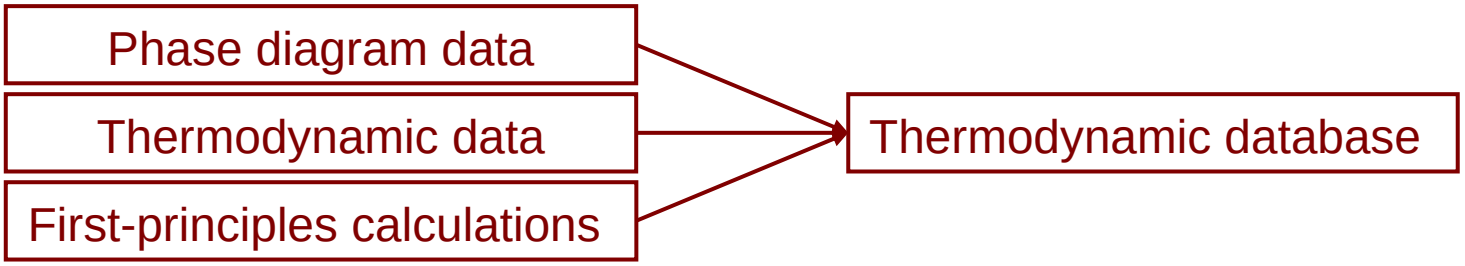
4. Summary

2.1 Thermodynamic database for cemented carbides

The C-Co-Fe-Ni-Cr-V-W-Ta-Ti-Nb-Zr-Mo-N system

Gibbs enegy as a function of composition, temperature and pressure



13 elements: Scientific Group Thermodata Europe (SGTE) database

78 binary systems: Assessed (7) or taken from the literature

286 ternary systems: Assessed (12) or taken from the literature

Assessed systems C–Cr–Ta,C–Cr–Nb, C–Ta–Ti,C–Ta–Nb, C–Ti–Nb, Co–Cr–Ti, C–Co–Cr, C–Co–Ta, C–Co–Ti, C–Co–Nb, C–W–Ta, and Co–Cr–W

315 qauternary systems: Assessed (8) or taken from the literature

Most important phases: WC, cubic carbides / carbonitrides, binder cubic (Co), graphite and eta (M6C) phases.

2.1 Thermodynamic database for cemented carbides

Phase diagram calculations

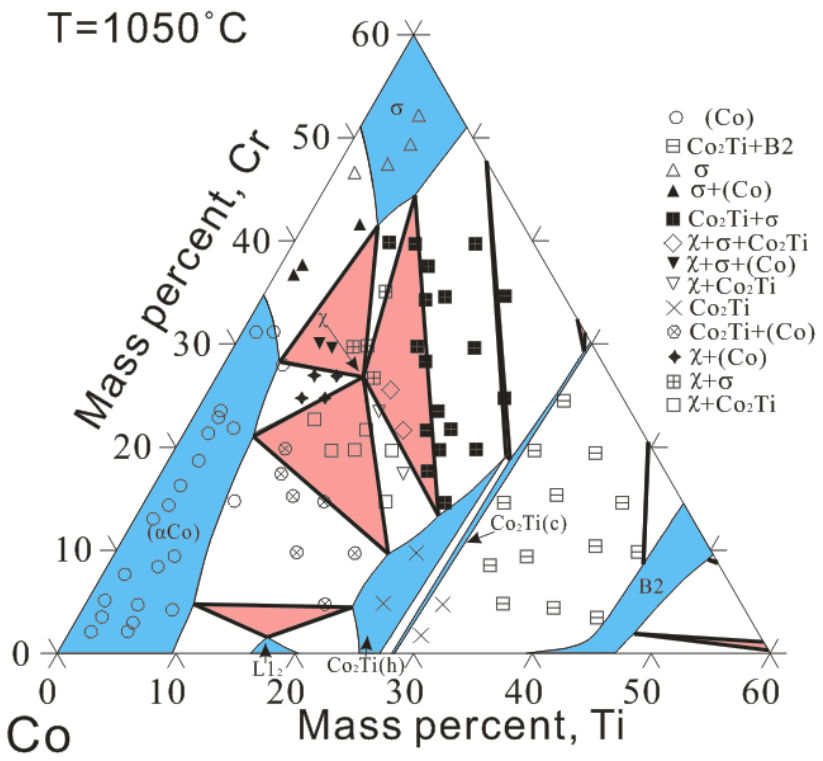


Fig. 1. Calculated Co-Cr-Ti isothermal sections at 1050°C.

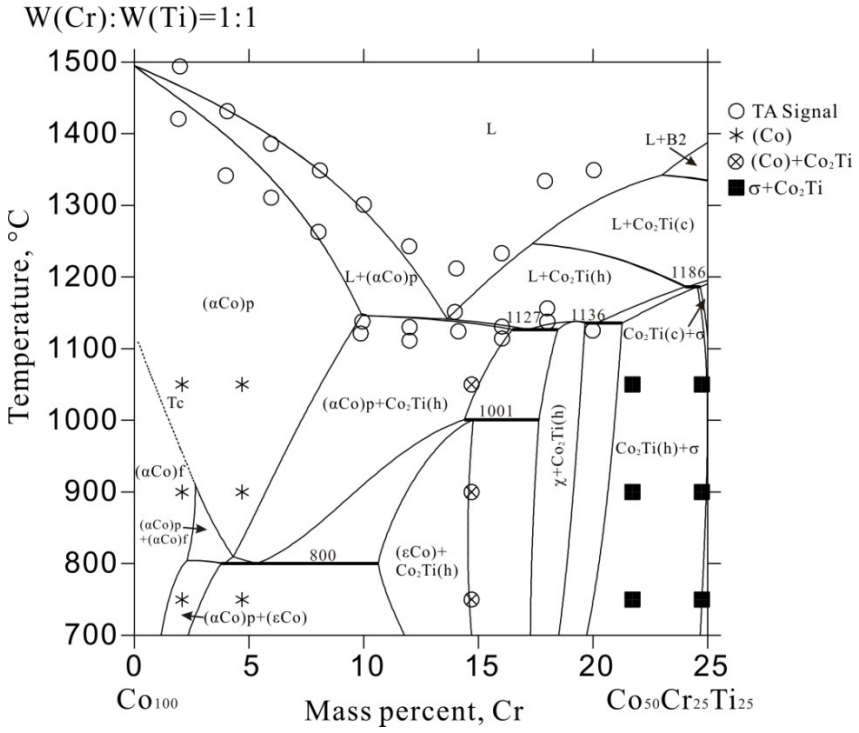


Fig. 2. Calculated vertical section along the line of w(Cr):w(Ti)=1:1, in comparison with the experimental data

- Y.B. Peng, Y. Du, et al., Int J Refract Met and Hard Mater, 42 (2014) 57–70

2.2 Diffusion database for cemented carbides

The C-Co-Cr-V-W-Ta-Ti-Nb-Zr-Mo-N system (11 elements)

- **Diffusion in liquid phase**

Theoritical prediction

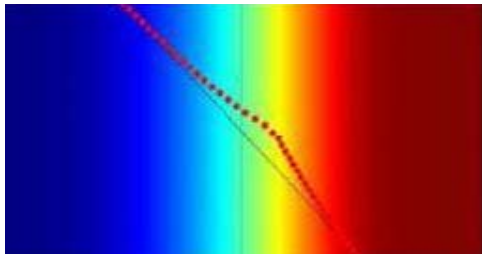
Difficult to measure due to convection and microgravity

Limit experimental data

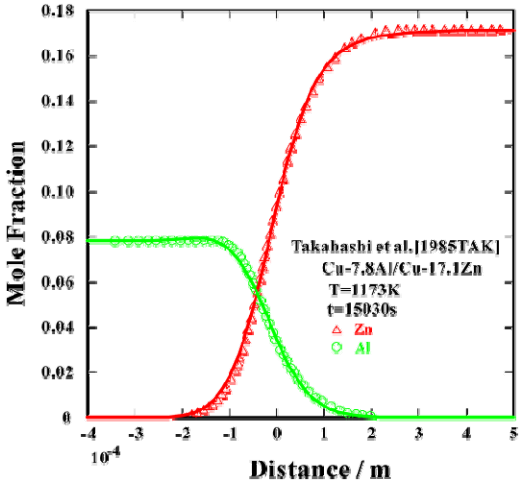
- **Diffusion in fcc phase**

Key experiment & modeling

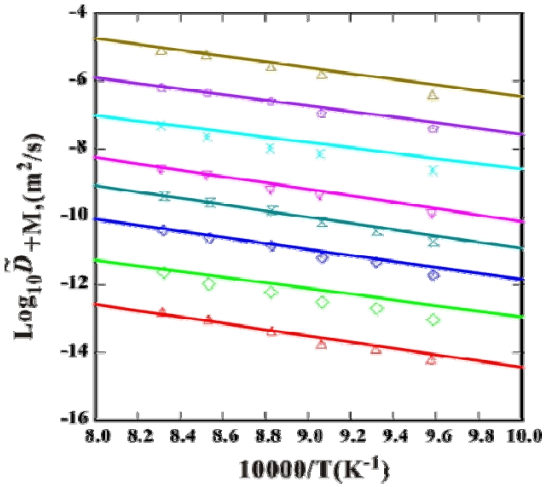
Annealed diffusion couple



EPMA Measurement



Diffusion coefficient calculation



2.2 Diffusion database for cemented carbides

- **Relation between D and M (atomic mobility)**

$$D_{kj}^{n} = \sum_{i} (\delta_{ik} - x_k) x_i M_i \left(\frac{\partial \mu_i}{\partial x_j} - \frac{\partial \mu_i}{\partial x_n} \right)$$

- **Atomic mobility expression**

$$M_i = \exp\left(\frac{RT \ln M_i^0}{RT} \right) \exp\left(\frac{-Q_i}{RT} \right) \frac{1}{RT} = \exp\left(\frac{\Delta G_i^*}{RT} \right) \frac{1}{RT}$$

- **Parameters in database**

$$\Delta G_i^* = \sum_j x_j \boxed{\Delta G_i^j} + \sum_j \sum_{k>j} x_j x_k \left[\sum_{r=0}^{m} \boxed{{}^r \Delta G_i^{j,k}} \left(x_j - x_k \right)^r \right] + \sum_j \sum_{k>j} \sum_{l>k} x_j x_k x_l \left[\sum_s v_{jkl}^s \boxed{{}^s \Delta G_i^{j,k,l}} \right] \ldots$$

Self- and impurity parameter Binary parameter Ternary parameter

Diffusivities are calculated from those of the sub-binary and sub-ternary alloys!

2.2 Diffusion database for cemented carbides

Self- and impurity diffusion coefficients in liquid phase

Modified Sutherland equation:

$$D = \frac{k_B T}{6\pi\mu r}\left(\frac{1+\frac{2\mu}{\beta r}}{1+\frac{3\mu}{\beta r}}\right)^{-1}$$

k_B, Boltzmanns constant

$$\mu_i = C_1 \frac{M_i^{1/2}}{V_i^{2/3}} T^{1/2} \exp\left(C_2 \frac{T_i^m}{T}\right)$$

Kaptay's viscosity formula

T^m, Melting temperature;

M, Mass;

$$r_i(T) = 0.644\times10^{-8}\left(\frac{M_i}{\rho_i^m}\right)^{1/3}\left(1-0.112\sqrt{\frac{T}{T_i^m}}\right)$$

Proptopapas's effective radius equation

ρ^m, Density at the melting point;

$$\beta = \begin{cases} 0 (r_A \le r_B) \\ \infty (r_A > r_B) \end{cases}$$

Sliding friction coefficient

r_A and r_B, Atomic radius of solute A and solvent B

- W.M. Chen, L.J. Zhang, Y. Du et al., Philosophical Magazine 94 (2014) 1552-1577

2.2 Diffusion database for cemented carbides

- This work (using the data of pure elements) does not need any diffusivity data
- DICTRA needs experimental and theoretical diffusivities
- Assumption in Frykholm: All elements have the same mobility (Q=65000, D_0=9.24*10^{-7})

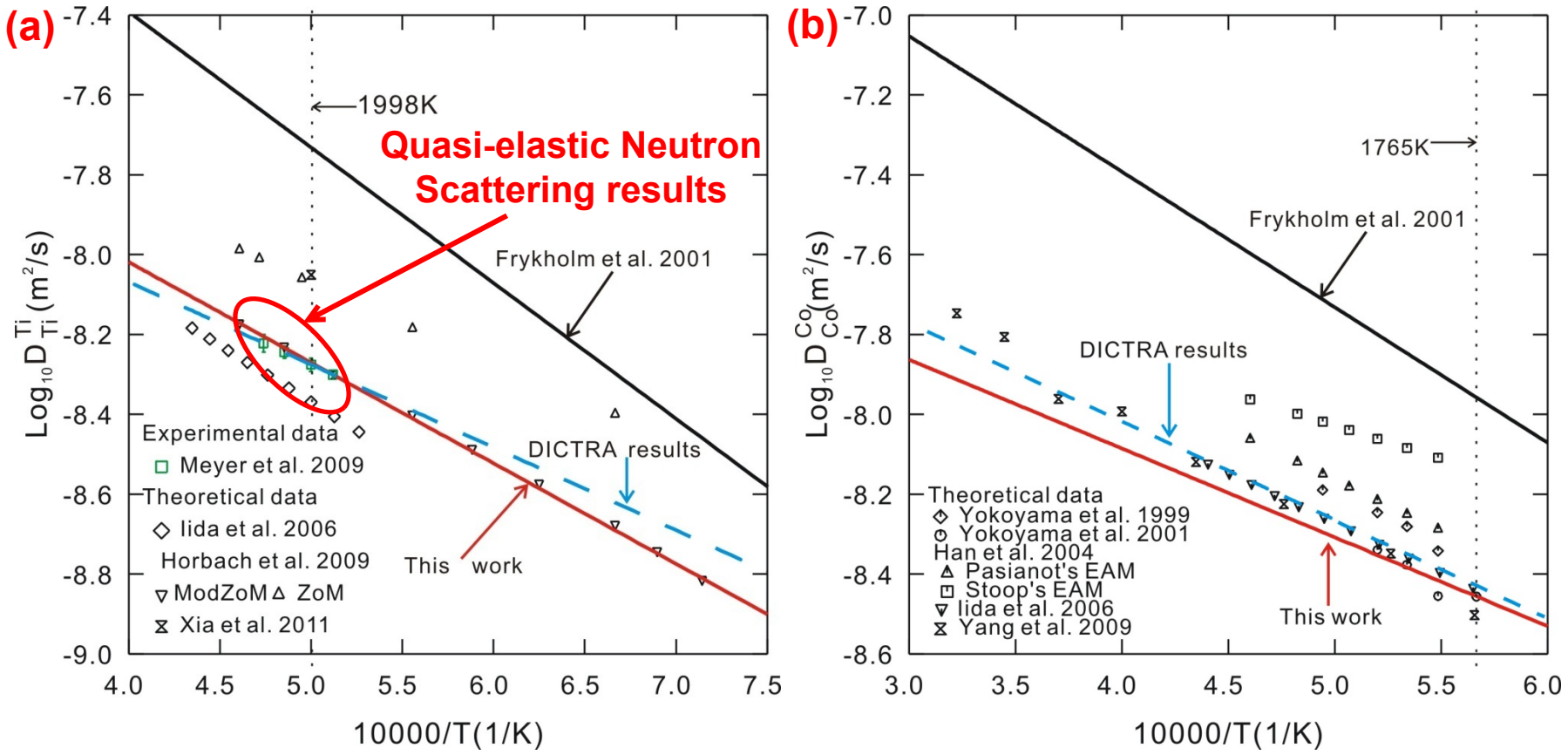


Fig. 3. Self-diffusivity of liquid (a) Ti and (b) Co

➢ W.M. Chen, L.J. Zhang, Y. Du et al., Philosophical Magazine 94 (2014) 1552-1577

2.2 Diffusion database for cemented carbides

Diffusivities in fcc Co-Cr-Nb-Ta-Ti-W alloys can be calculated from those of the sub-binary alloys.

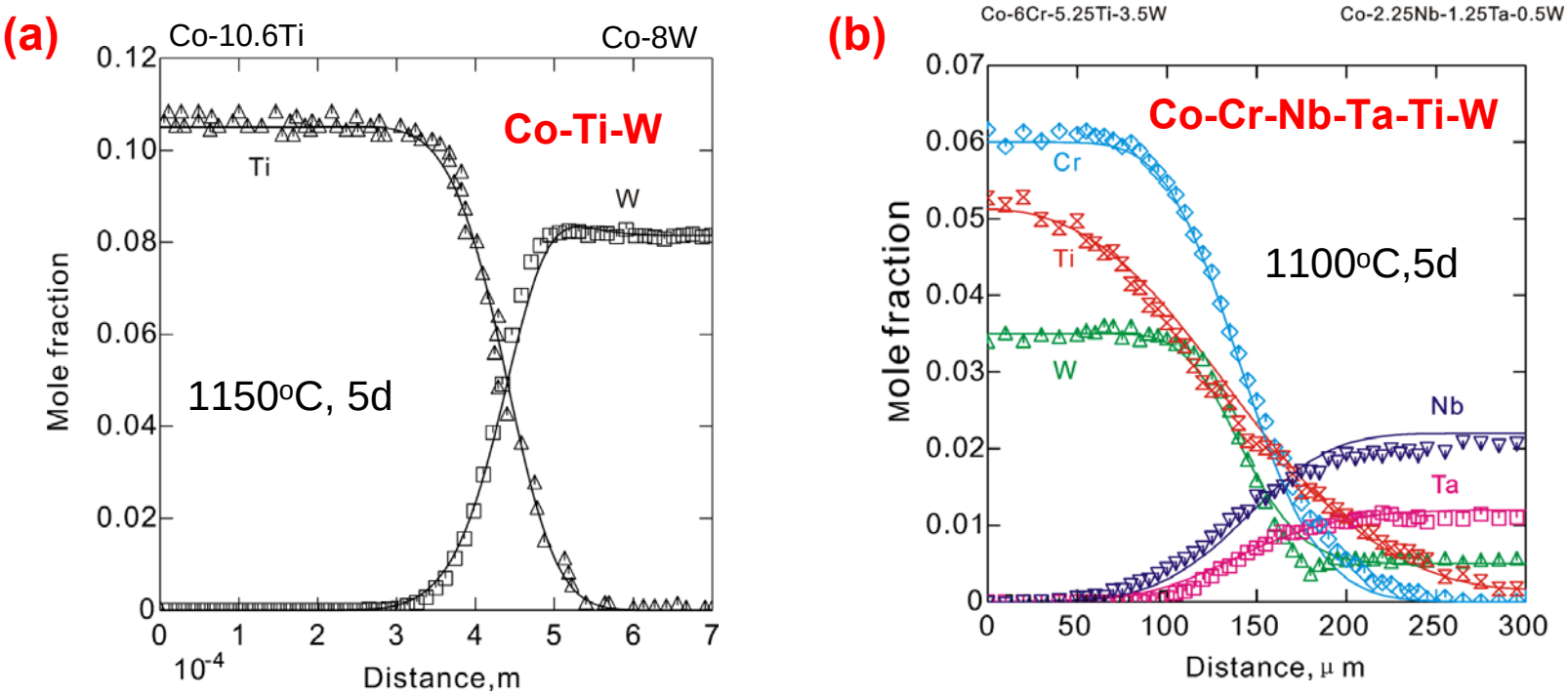


Fig. 4. Calculated and measured concentration profiles of

(a) Co-10.6Ti // Co-8W diffusion couples and **(b)** Co-6Cr-5.25Ti-3.5 W // Co-2.25Nb-1.25Ta-0.5W

- **W.B. Zhang, Y. Du, et al., Int. J. Refract Met Hard Mater., 43,164-180 (2014).**

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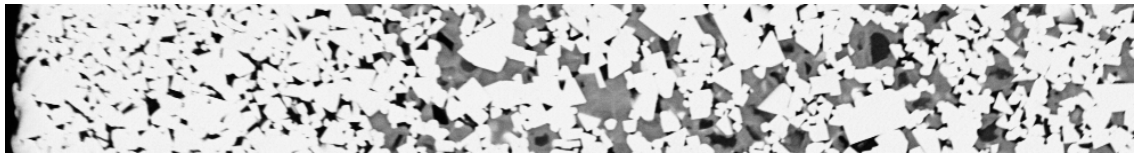
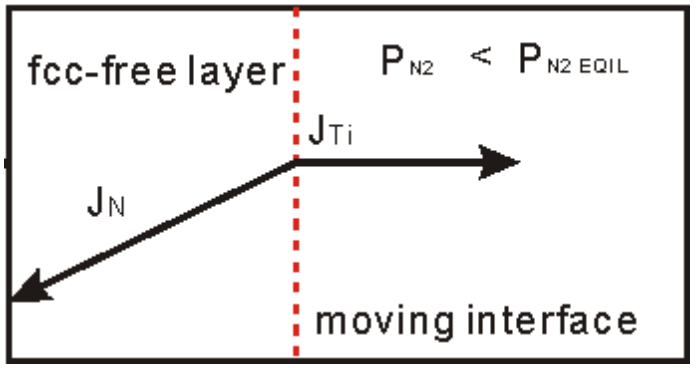
3.1 1D simulation of Gradient cemented carbide

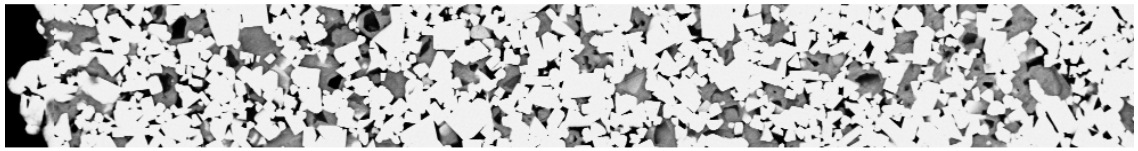
Nitrogen gas pressure:Control the type of metallurgical reactions and rearrangement of the elements during sintering (microstructure evolution)

$P<P_{equil}$ **Denitrification**

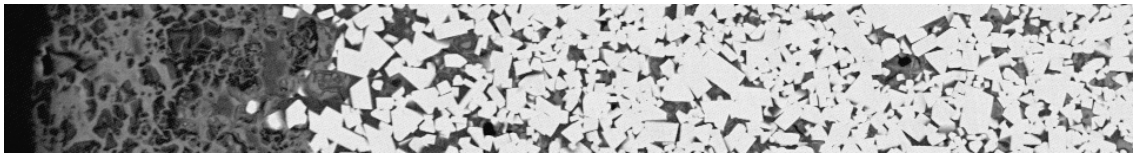


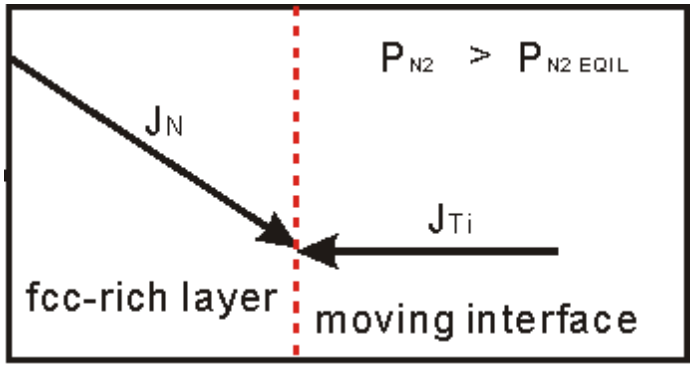


$P=P_{equil}$ **Nitrogen equilibrium**



$P>P_{equil}$ **Nitrification**





3.1 1D simulation of Gradient cemented carbide

$P<P_{equil}$ **Denitriding**

W-7.5Co-5Ti-6.35C-0.1N, 1450ºC, 1h

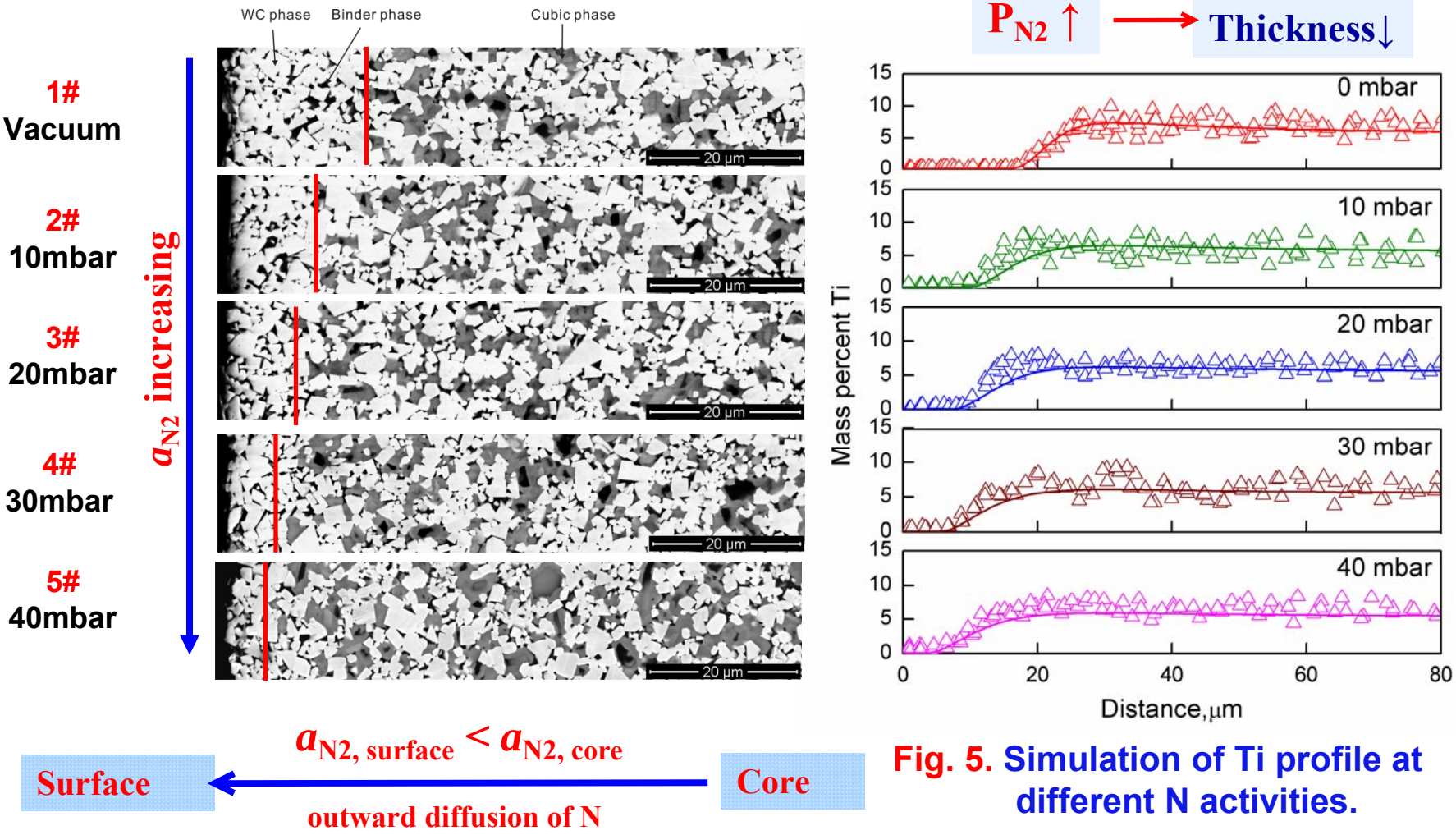


Fig. 5. Simulation of Ti profile at different N activities.

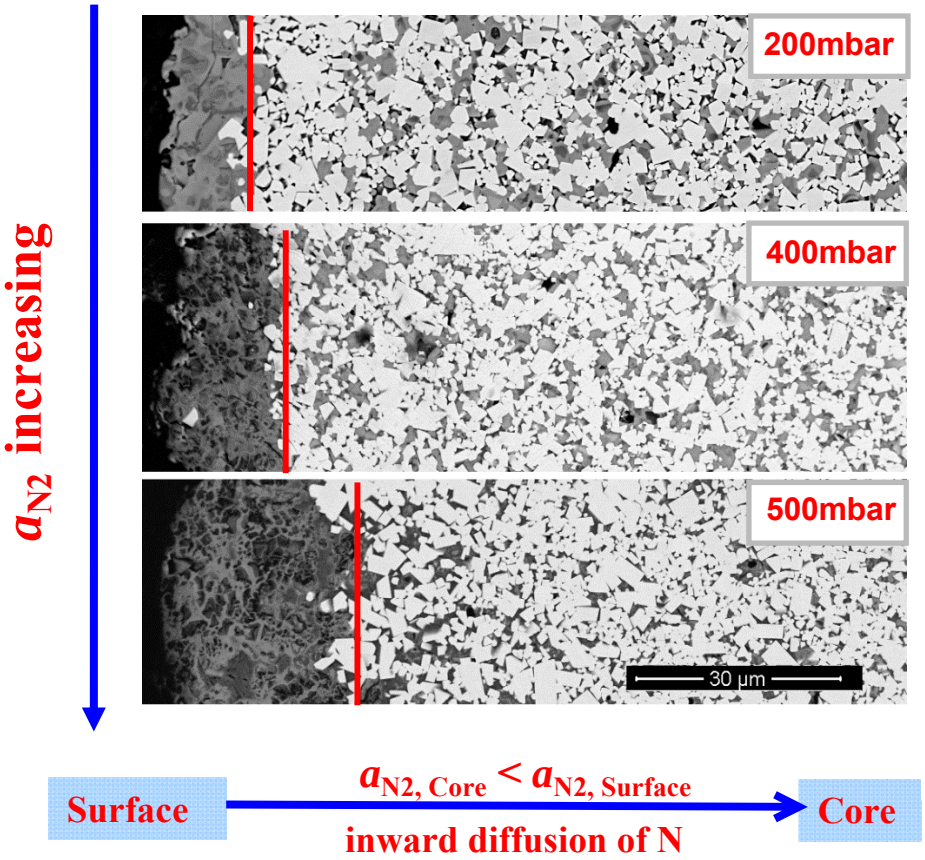
➢ **W.B. Zhang, Y. Du, et al., Int. J. Refract Met Hard Mater., 43,164-180 (2014).**

3.1 1D simulation of Gradient cemented carbide

$P>P_{equil}$ **Nitriding**

W-7.5Co-5Ti-6.35C-0.1N, 1450ºC, 1h

P_{N2} ↑ → **Thickness↑**



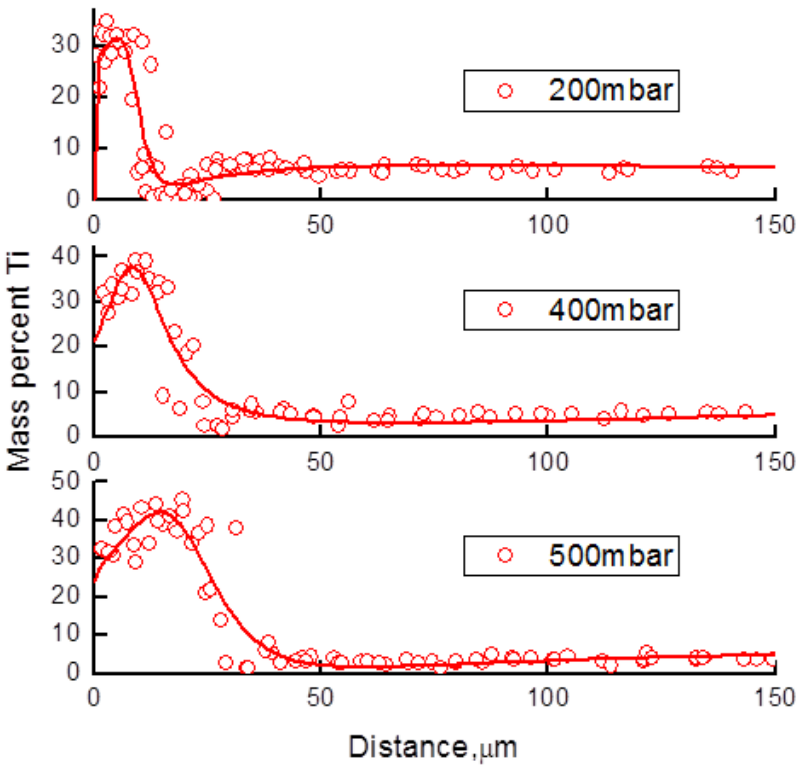
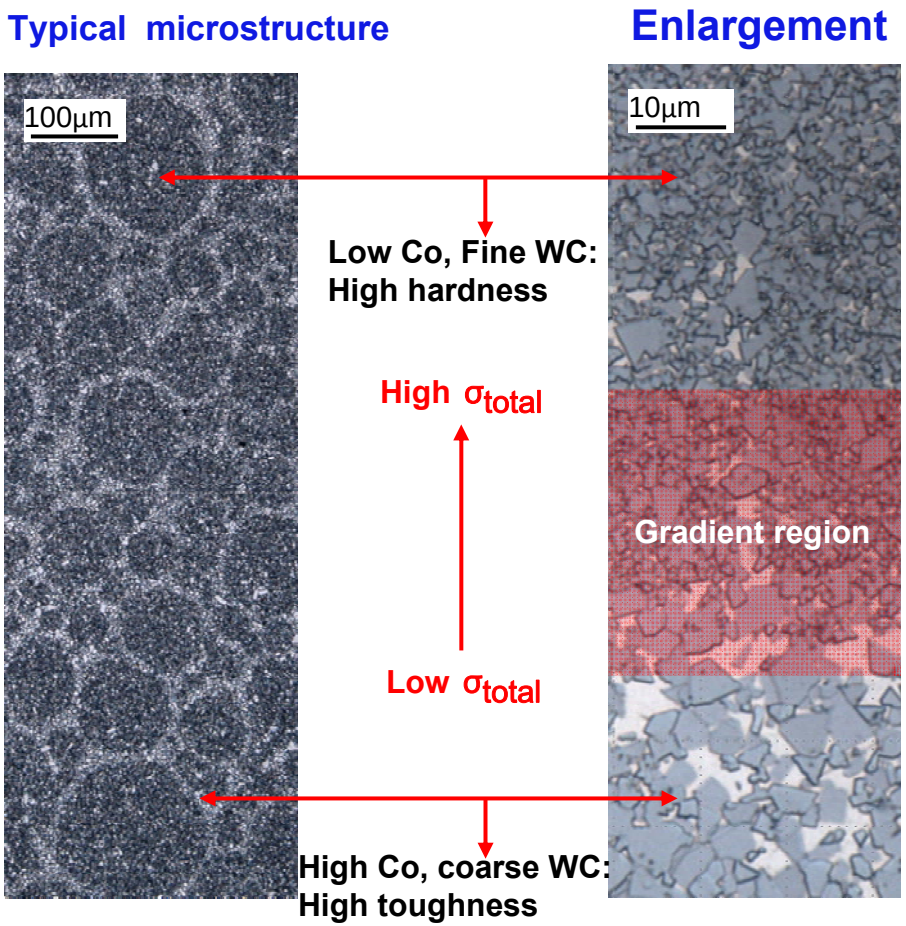


Fig. 6. Simulation of Ti profile at different N activities.

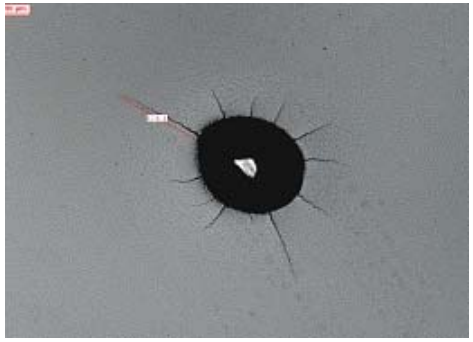
- **W.B. Zhang, Y. Du, et al., Int. J. Refract Met Hard Mater., 43,164-180 (2014).**

3.2 1D and 2D simulation of Cellular cemented carbide

Cellular cemented carbide:



- Superior combination of wear resistance and fracture toughness



Prevent crack propagation

- Migration rule during liquid sintering:

  High Co → Low Co

  Coarse WC → Fine WC

  Low σ_{total} → High σ_{total}

- During sintering, binder phase migration driven by total interface energy (σ_{total})

3.2 1D and 2D simulation of Cellular cemented carbide

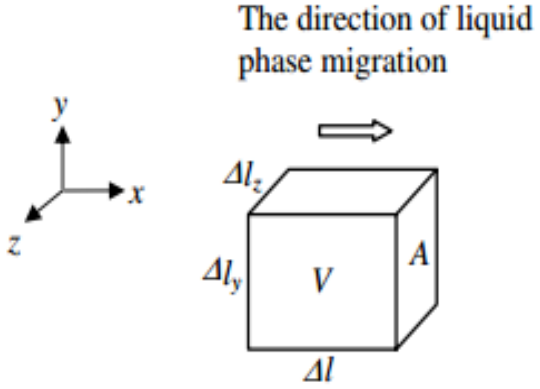
1D simulation: Governing equation

- **Case A: Only binder migration**

The binder volume evolution equation developed by Fan et al. [1]

Volume conservation:

$$\frac{dV_l}{dt} = -\Delta l \cdot \frac{\partial}{\partial x}(v \cdot A)$$



Final equation:

$$A_0 \times (1-u_0)^{2/3} \times \boxed{\frac{\partial (1-u)^{-2/3}}{\partial t}} = -\frac{2}{3} \times \frac{\partial}{\partial l}\left(\frac{k_p}{\mu}\left(\frac{1-u_0}{1-u}\right)^{2/3} A_0 \boxed{\frac{\partial P_m}{\partial l}} + \frac{k_p}{\mu}\left(\frac{1-u_0}{1-u}\right)^{2/3} A_0 \boxed{\frac{\partial^2 P_m}{\partial l^2}} \right)$$

Volume evolution **Driving force** $P_m = 2048 \times \left[(1/u - 1)^{1/3} - 1.41 \times u \right] / d^{0.4}$

where A_0 is the cross sectional area, u_0 is the initial volume fraction of liquid phase, l is the distance, k_p is the permeability, μ is the viscosity of liquid phase and P_m is the liquid migration pressure.

➢ **P. Fan, Z.Z. Fang, H.Y. Sohn, Acta Materialia, 55, 3111-3119 (2007).**

3.2 1D and 2D simulation of Cellular cemented carbide

1D simulation: Governing equation

- **Case B: Migration + Diffusion**

Coupling concentration evolution equation (Fick's second law)

$$A_0 \times (1-u_0)^{2/3} \times \frac{\partial (1-u)^{-2/3}}{\partial t} = -\frac{2}{3} \times \frac{\partial}{\partial l}\left(\frac{k_p}{\mu}\left(\frac{1-u_0}{1-u}\right)^{2/3} A_0 \right) \frac{\partial P_m}{\partial l} - \frac{k_p}{\mu}\left(\frac{1-u_0}{1-u}\right)^{2/3} A_0 \frac{\partial^2 P_m}{\partial l^2}$$

$$\frac{dC_{Co}}{dt} = \tilde{D}\frac{\partial^2 C_{Co}}{\partial x^2}$$

where *D* is the interdiffusion coefficient of binder in liquid state.

Thermodynamic database:

Relationship between mass fraction and volume fraction (u-C_{Co}) at 1673K.

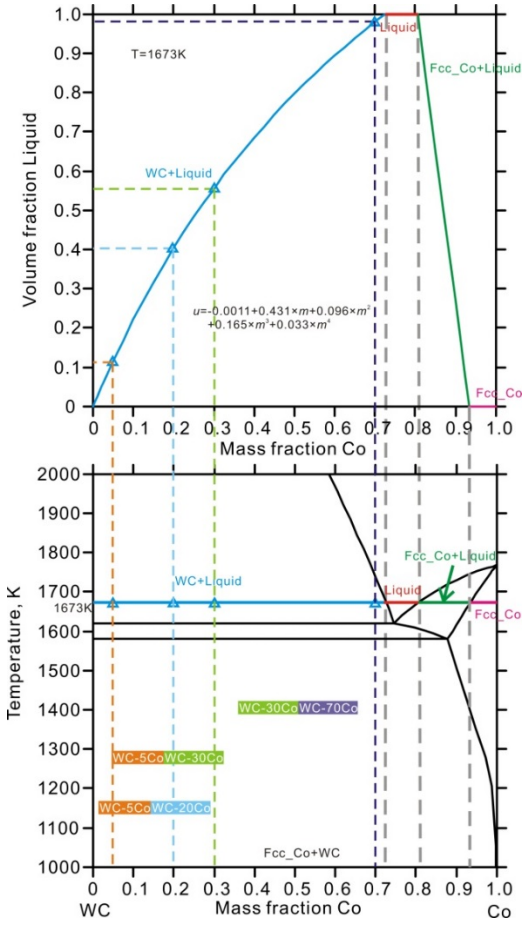


Fig. 7. calculation of u-C relation .

➢ **K.M. Cheng, T. Xu, Y. Du et al., Int. J. Refract Met Hard Mater., 42,180-184 (2014).**

3.2 1D and 2D simulation of Cellular cemented carbide

1D Numerical Simulation Results

- **Case A: Only binder migration**

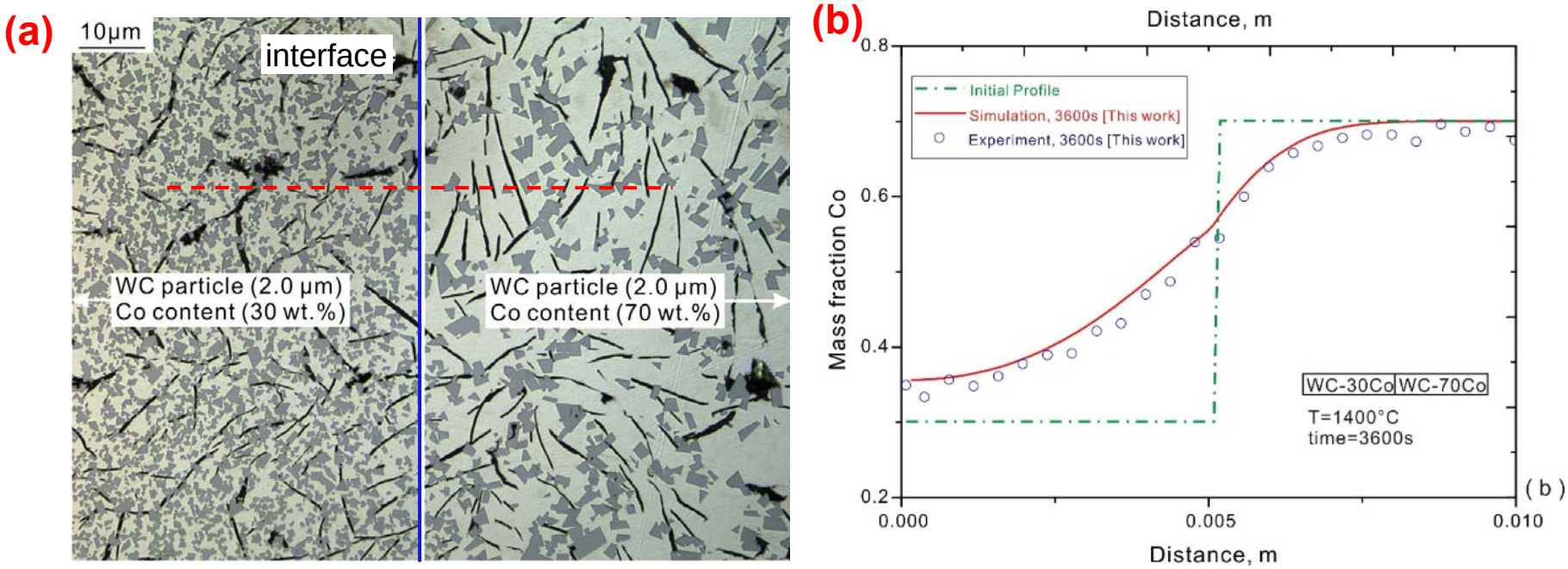


Fig. 8. (a) SEM images of the diffusion couples and (b) Simulated Co profile with the experiment (1400C for 1 h)

- **K.M. Cheng, T. Xu, Y. Du et al., Int. J. Refract Met Hard Mater., 42,180-184 (2014).**

3.2 1D and 2D simulation of Cellular cemented carbide

1D Numerical Simulation Results

- **Case B: Migration + Diffusion**

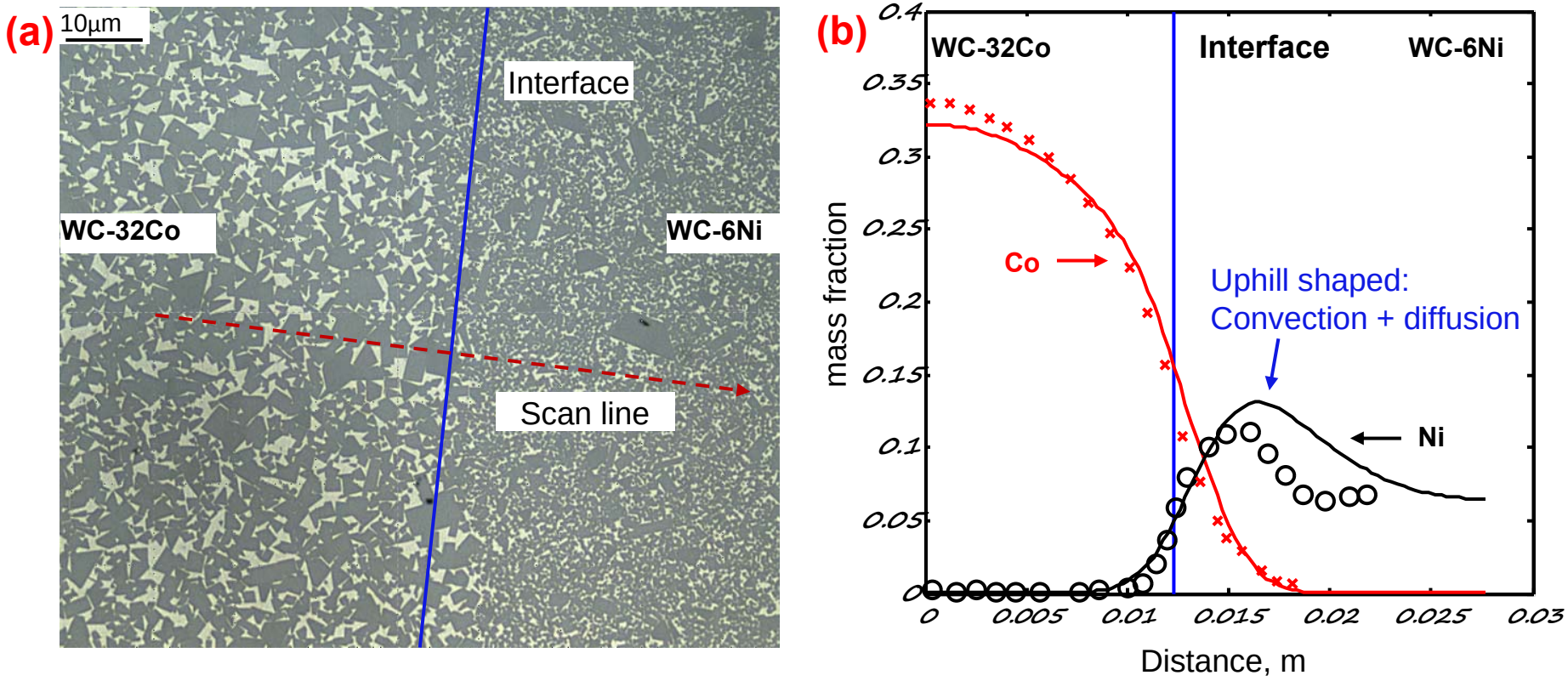


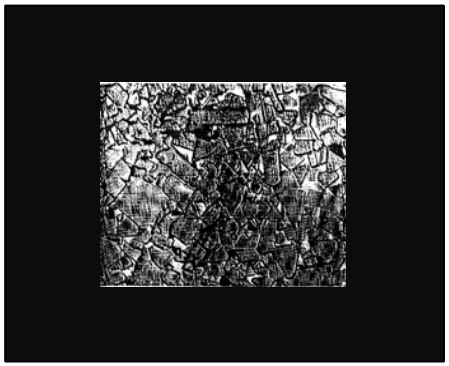
Fig. 9. (a) SEM images of the diffusion couples and (b) Simulated Co and Ni profiles with the experiment (1400 C for 6 minutes)

- **K.M. Cheng, Y. Du et al., Unpublished work (2014).**

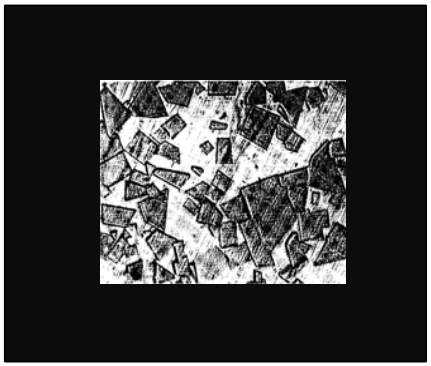
3.2 1D and 2D simulation of Cellular cemented carbide

2D simulation

Experiment

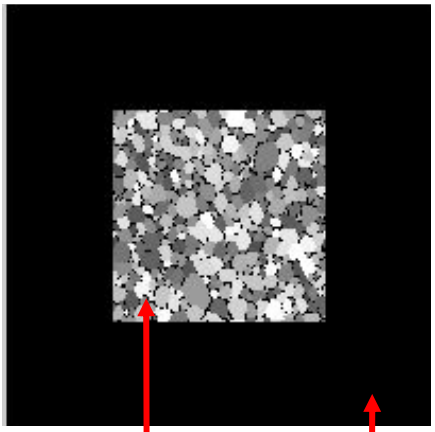


Initial: WC-6Co in Liquid Co



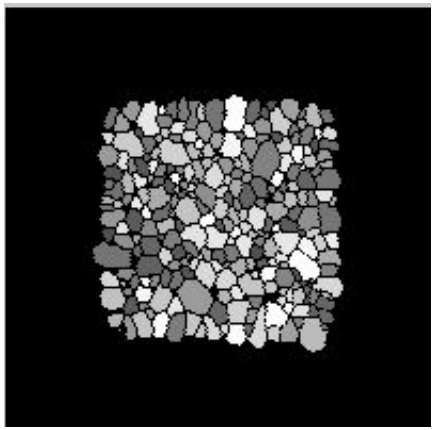
Stable content: 32Co

Preliminary simulation



Initial: WC-6Co

Liquid Co



Stable content: 17Co

Driving force:

- total interfacial energy.

Mechanism:

- solution and dissolution of WC
- Liquid flow

.

Present simulation:

Only considers solution and dissolution of WC .

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    2.2 Diffusion database
3. Simulation of microstructure in cemented carbides
    3.1 1D simulation of Gradient cemented carbide
    3.2 1D and 2D simulation of Cellular cemented carbide
4. Summary

4. Summary

- **The thermodynamic and diffusion databases for cemented carbides containing C-Co-Fe-Ni-Cr-V-W-Ta-Ti-Nb-Zr-Mo-N have been established.**

- **The microstructure evulation in gradient cemented carbide and cellular cemented carbide was simulated, and a good agreement between simulation and experiment is obatined.**

New databases for cemented carbides

CSUTDCC1 ⟶ **Thermodynamic database**

- **Y.B. Peng, Y. Du, et al., Int J Refract Met and Hard Mater, 42, 57–70 (2014)**

CSUDDCC1 ⟶ **Diffusion database**

- **W.B. Zhang, Y. Du, et al., Int. J. Refract Met Hard Mater., 43,164-180 (2014)**

More information: http://www.imdpm.net

Thank you for your attention !

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