The Influence of Contamination on the Thermal and Phase Stability of Nanocrystalline Ni-W Alloys

Chris Marvel, Denise Yin, Patrick Cantwell, Martin Harmer

International Workshop in
Interfaces at Bear Creek
2015

LEHIGH
UNIVERSITY

Office of Naval Research
ONR
Science & Technology

Grain Boundary Velocity

Must stop grain growth!

$$\underbrace{v}_{\text{GB Velocity}} \propto \underbrace{M}_{\text{GB Mobility}} \overbrace{\overset{\text{Energetic}}{\gamma}\,\overset{\text{Physical}}{\kappa}}^{\text{Grain Growth Driving Forces}}$$

Two Strategies

“Thermodynamic”

“Kinetic”

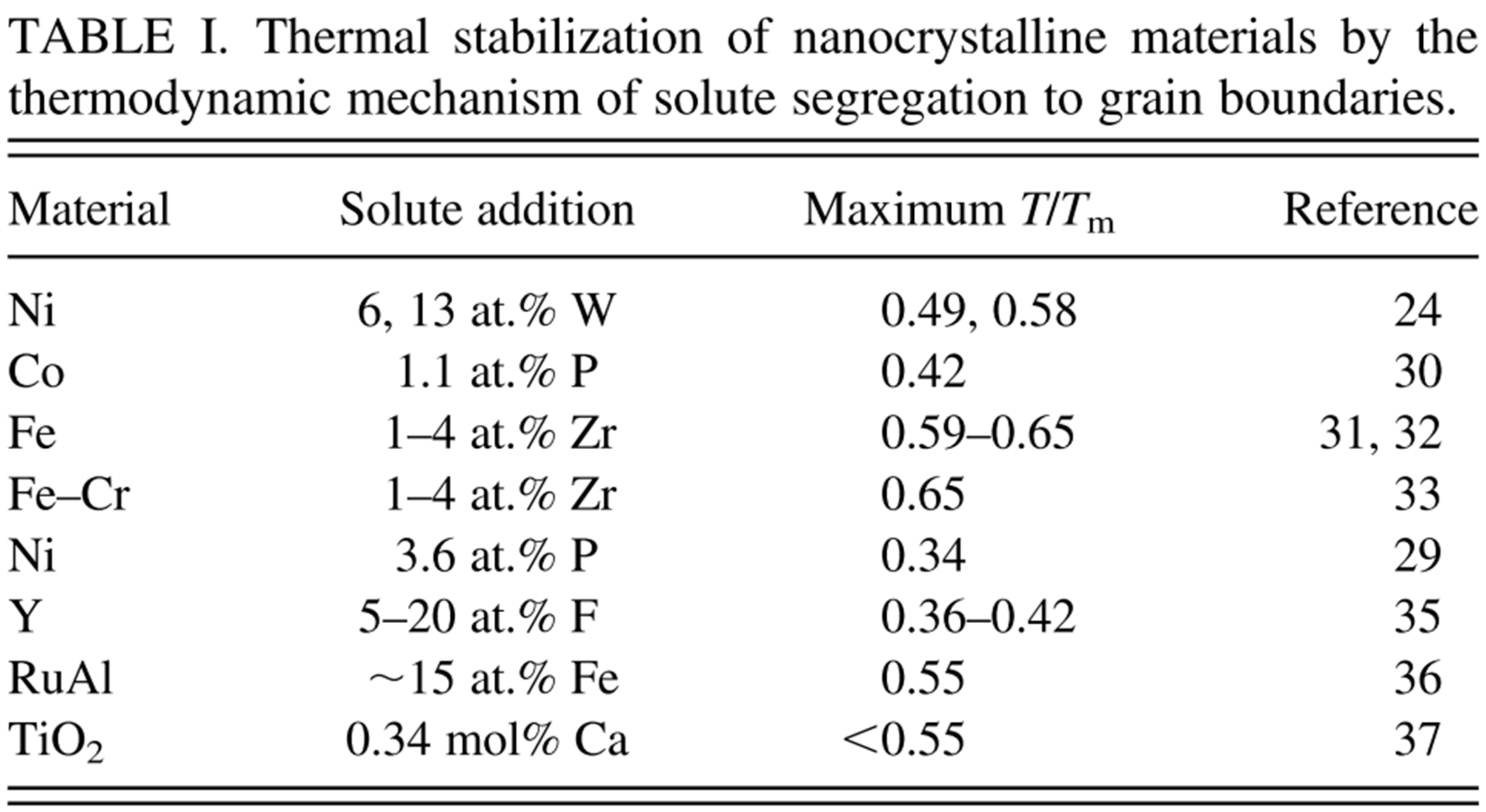


TABLE I. Thermal stabilization of nanocrystalline materials by the thermodynamic mechanism of solute segregation to grain boundaries.

Material	Solute addition	Maximum T/T_m	Reference
Ni	6, 13 at.% W	0.49, 0.58	24
Co	1.1 at.% P	0.42	30
Fe	1–4 at.% Zr	0.59–0.65	31, 32
Fe–Cr	1–4 at.% Zr	0.65	33
Ni	3.6 at.% P	0.34	29
Y	5–20 at.% F	0.36–0.42	35
RuAl	~15 at.% Fe	0.55	36
TiO_2	0.34 mol% Ca	<0.55	37

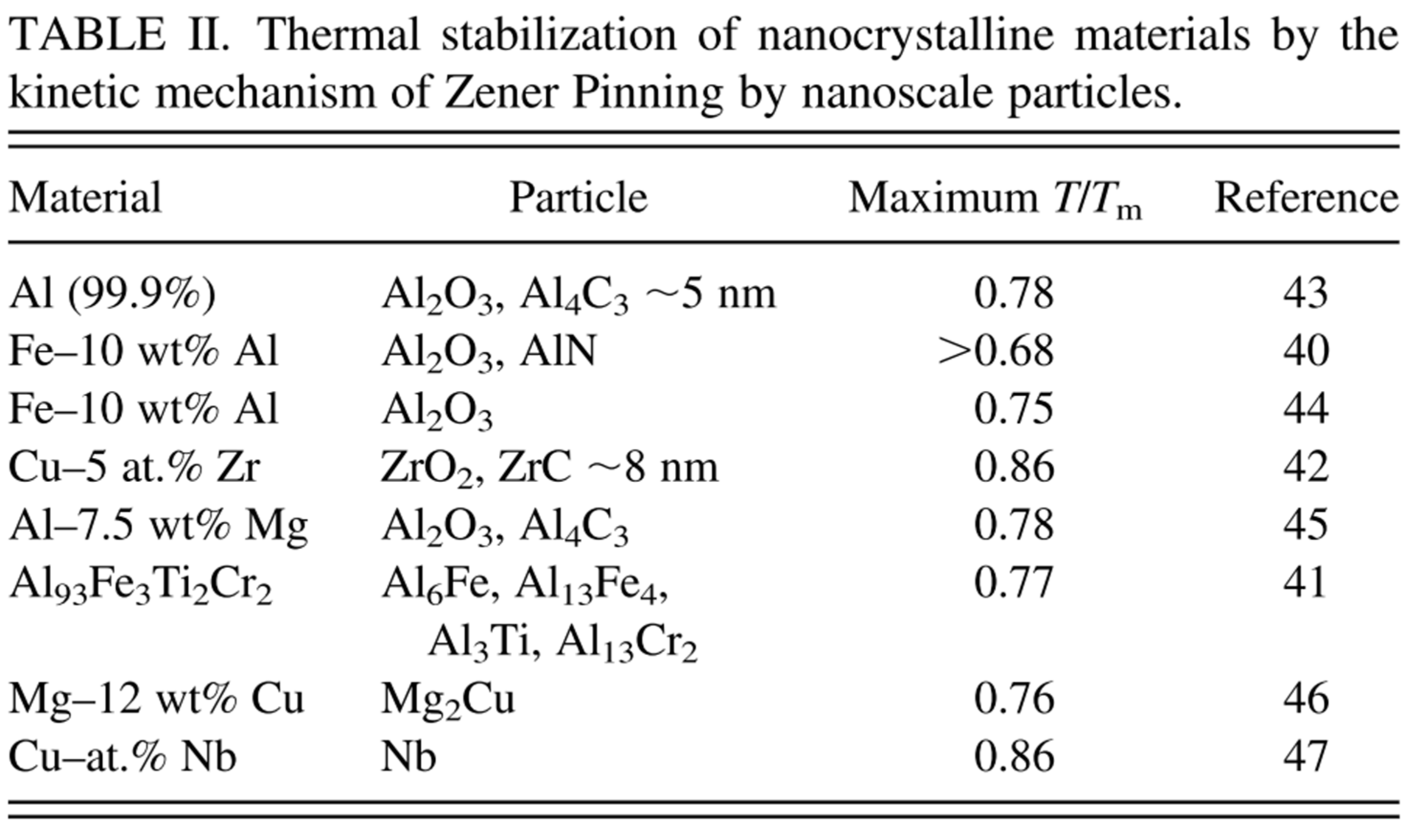


TABLE II. Thermal stabilization of nanocrystalline materials by the kinetic mechanism of Zener Pinning by nanoscale particles.

Material	Particle	Maximum T/T_m	Reference
Al (99.9%)	Al_2O_3, Al_4C_3 ~5 nm	0.78	43
Fe–10 wt% Al	Al_2O_3, AlN	>0.68	40
Fe–10 wt% Al	Al_2O_3	0.75	44
Cu–5 at.% Zr	ZrO_2, ZrC ~8 nm	0.86	42
Al–7.5 wt% Mg	Al_2O_3, Al_4C_3	0.78	45
$Al_{93}Fe_3Ti_2Cr_2$	Al_6Fe, $Al_{13}Fe_4$, Al_3Ti, $Al_{13}Cr_2$	0.77	41
Mg–12 wt% Cu	Mg_2Cu	0.76	46
Cu–at.% Nb	Nb	0.86	47

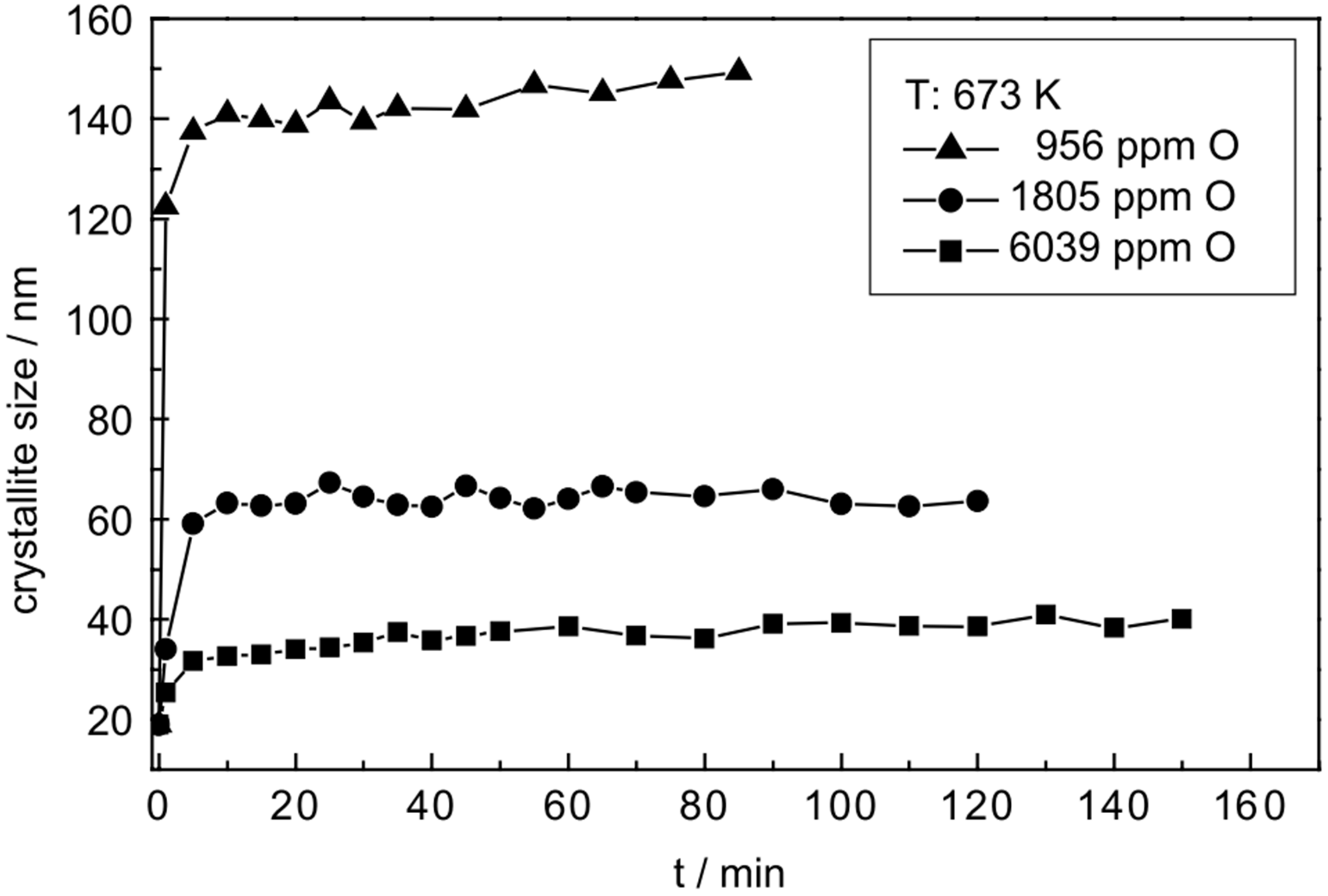
Ni-W and Ni-P Alloys

Impurity Particles...

Koch CC, Scattergood RO, Saber M, Kotan H. J Mater Res 2013;28:1785.

Processing Impurities

Oxygen from plating



Natter H, Hempelmann R. Electrochim. Acta 2003; 49

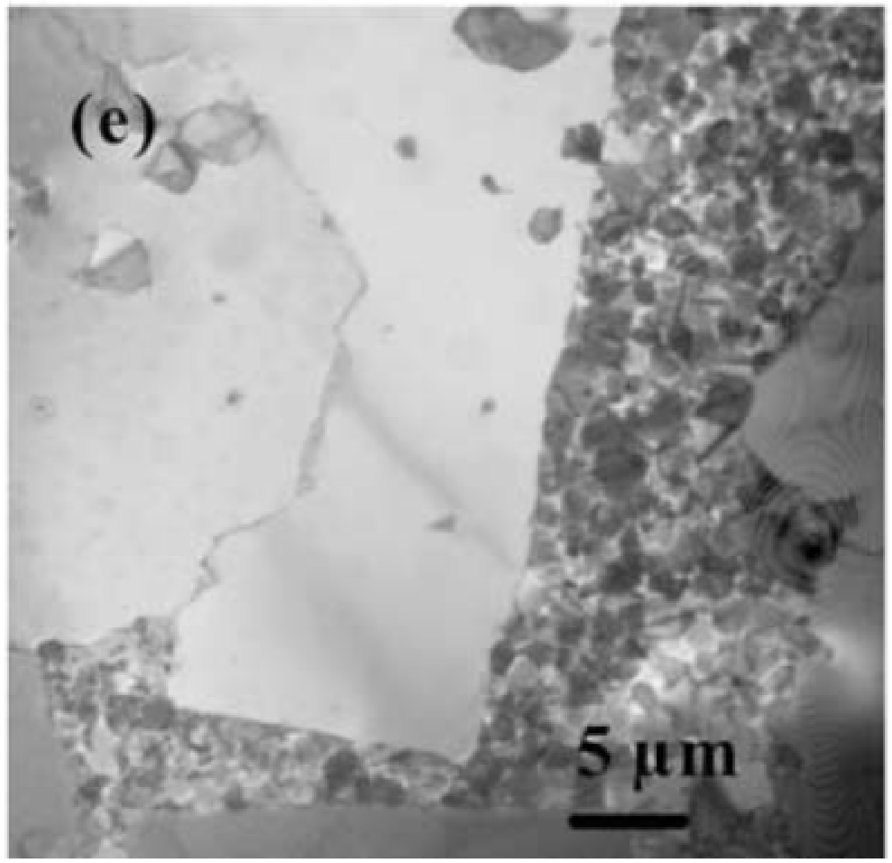
j_p (mA/cm^2)	t_{on} (ms)	t_{off} (ms)
50	–	–
5	–	–
1	–	–
250	2	8
100	5	95
5	2	8

H (ppm)	C (ppm)	O (ppm)	S (ppm)	Cl (ppm)
1	5	25	<1	<1
≈70	*≈100*	*≈400*	6	*×230*
≈130	*≈400*	*≈1000*	25	*×1000*
1	10	20	<1	<1
≈30	*≈100*	*≈400*	2	*×180*
≈96	*≈400*	*≈1000*	11	*×1000*

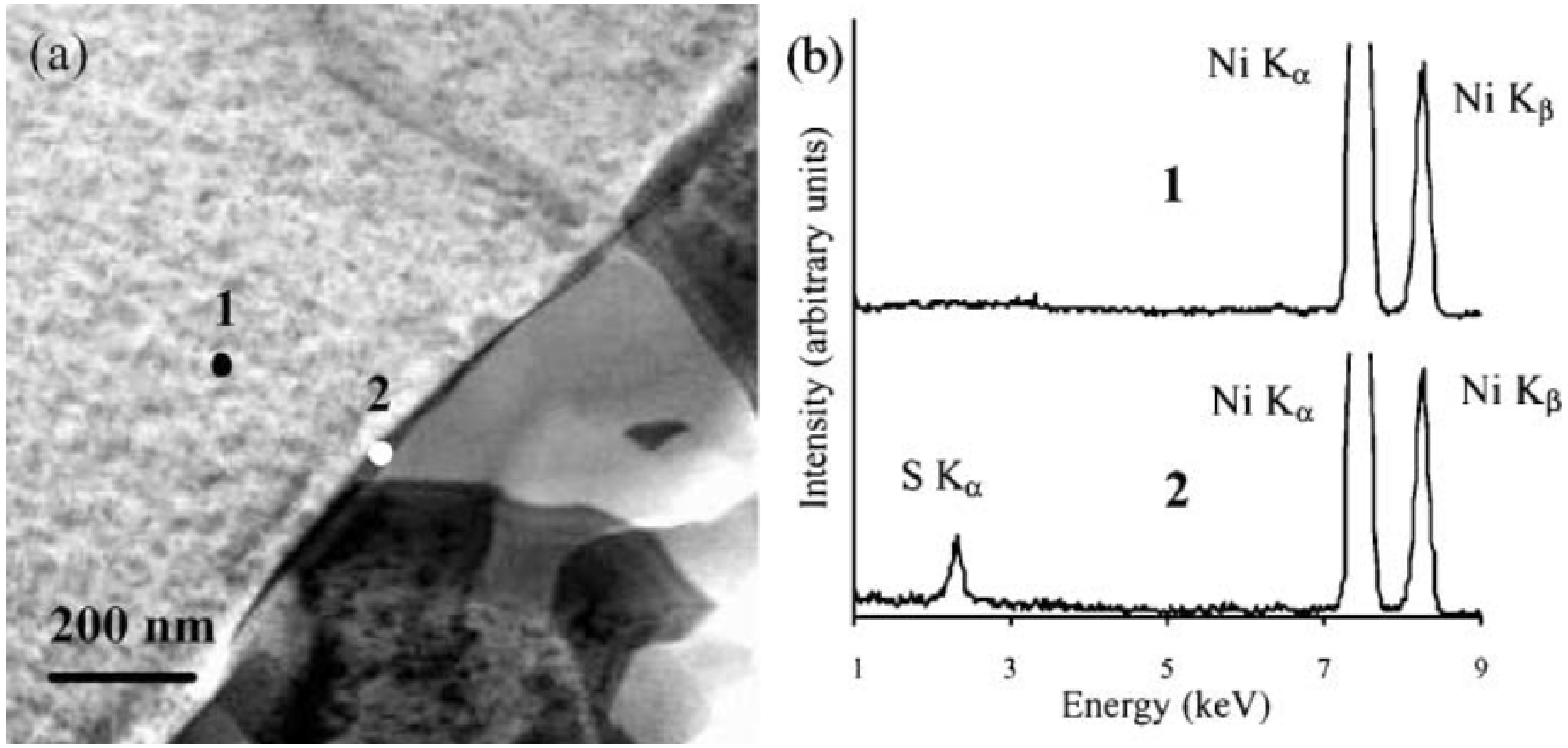
Modified from Savall C, Godon A., Creus J, Feaugas X. Surf. Coatings Technol. 2012; 206

Impurity Sulfur in Ni

420°C - 11 Hr



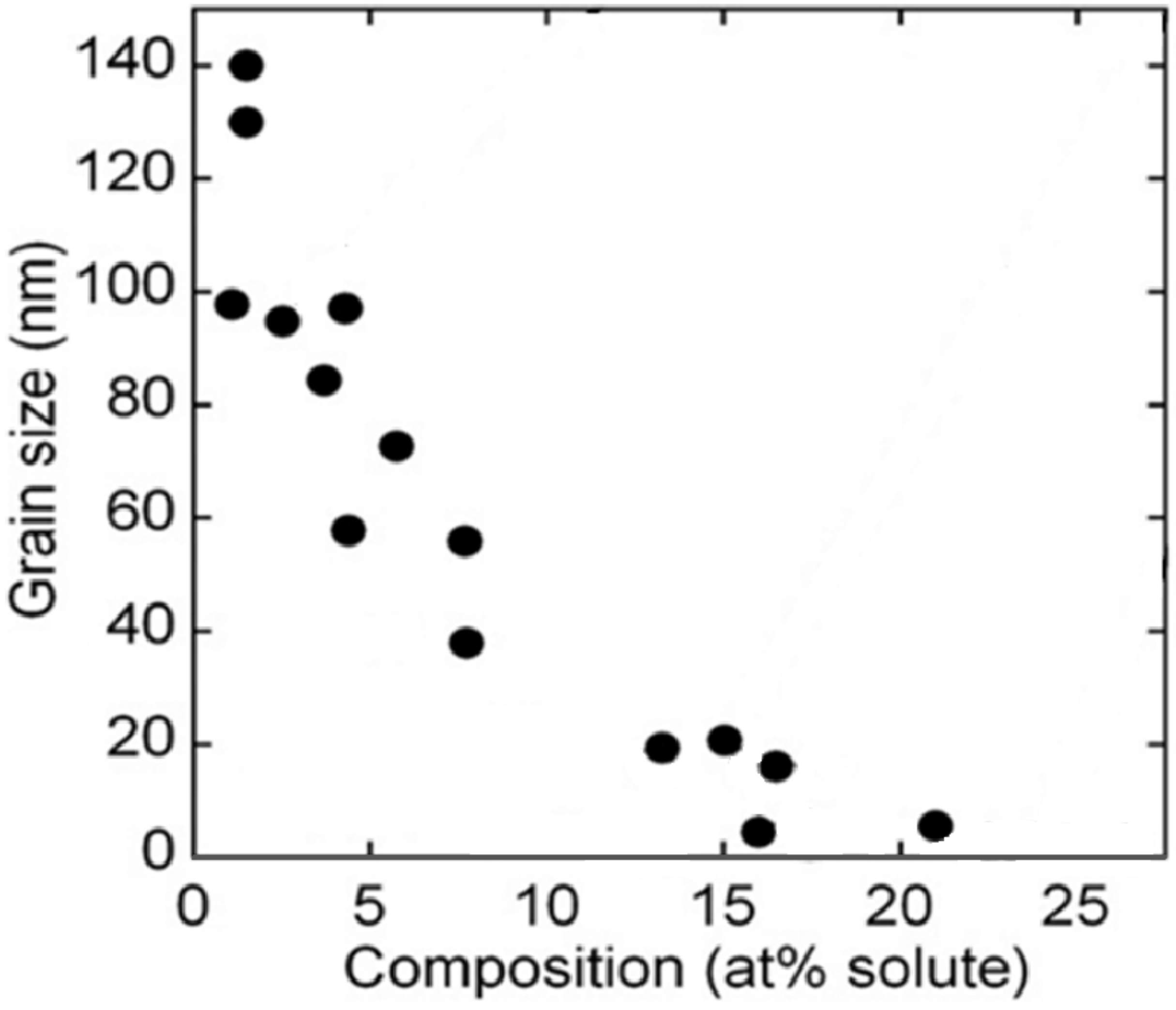
Grain Boundary EDS



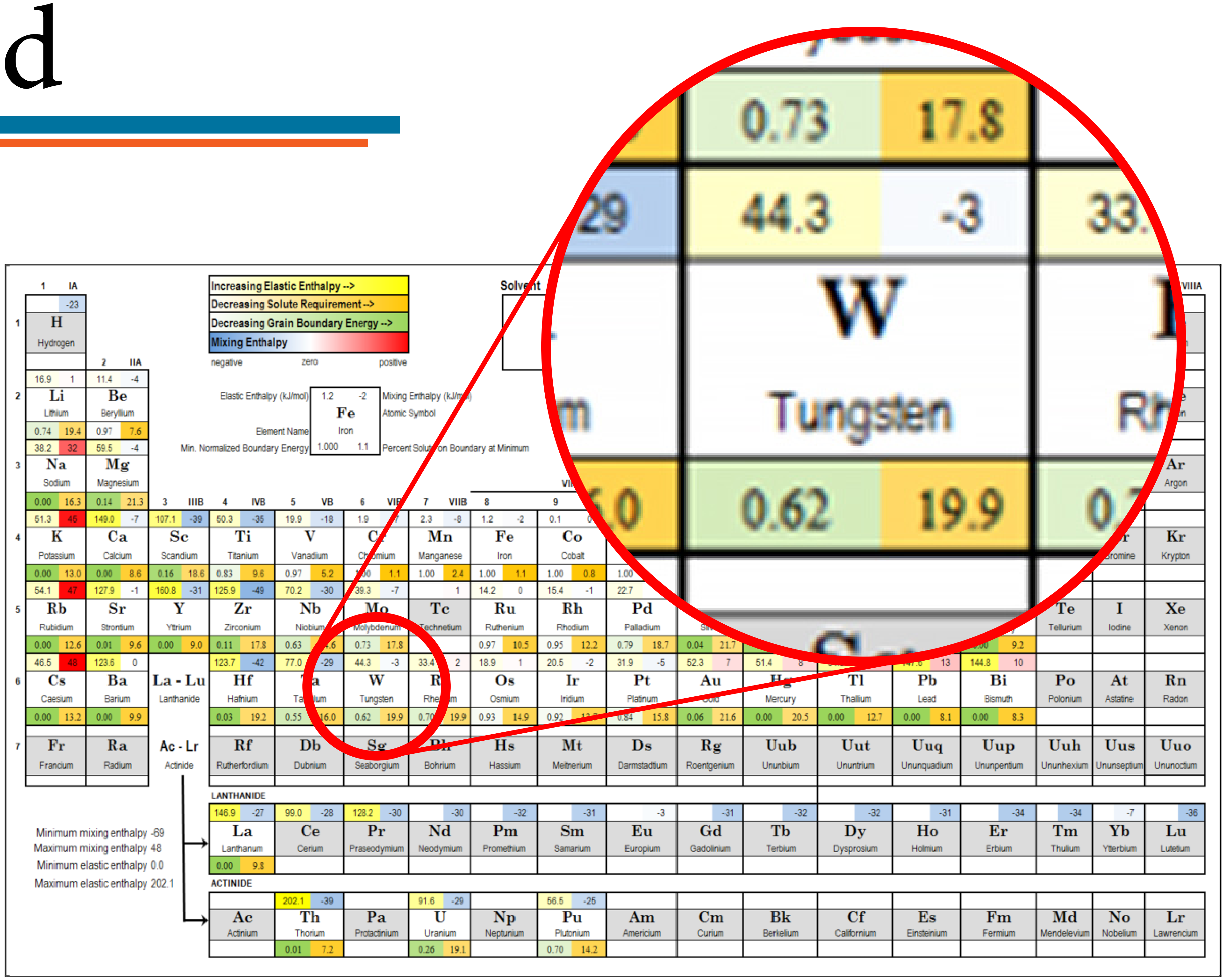
G.D. Hibbard, J.L. McCrea, G. Palumbo, K.T. Aust, U. Erb, Scr. Mater. 47 (2002) 83–87.

How often does segregation *increase* grain growth rate?

Ni-W Background

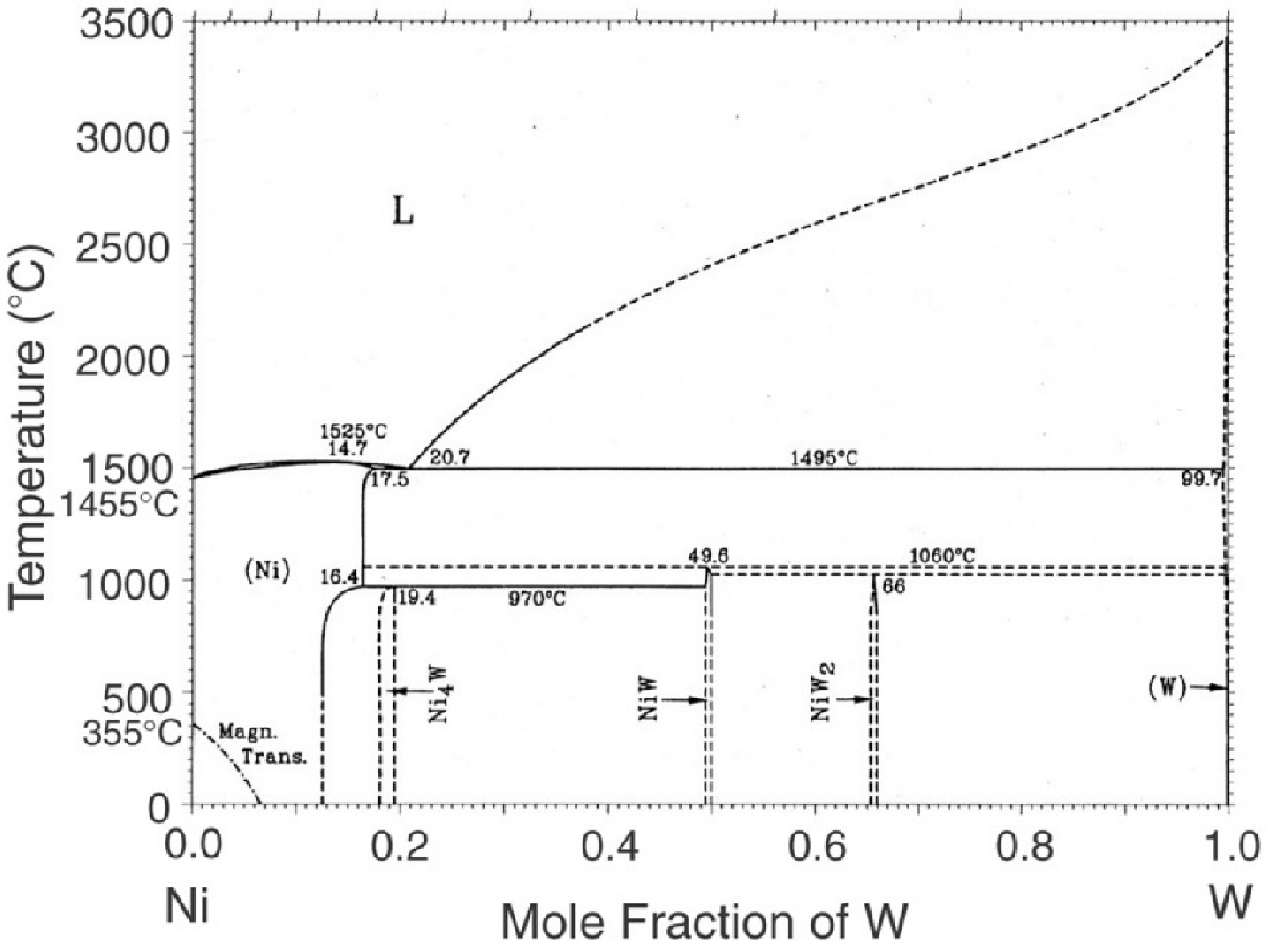


Detor AJ, Schuh CA. Acta Mater 2007;55:371.



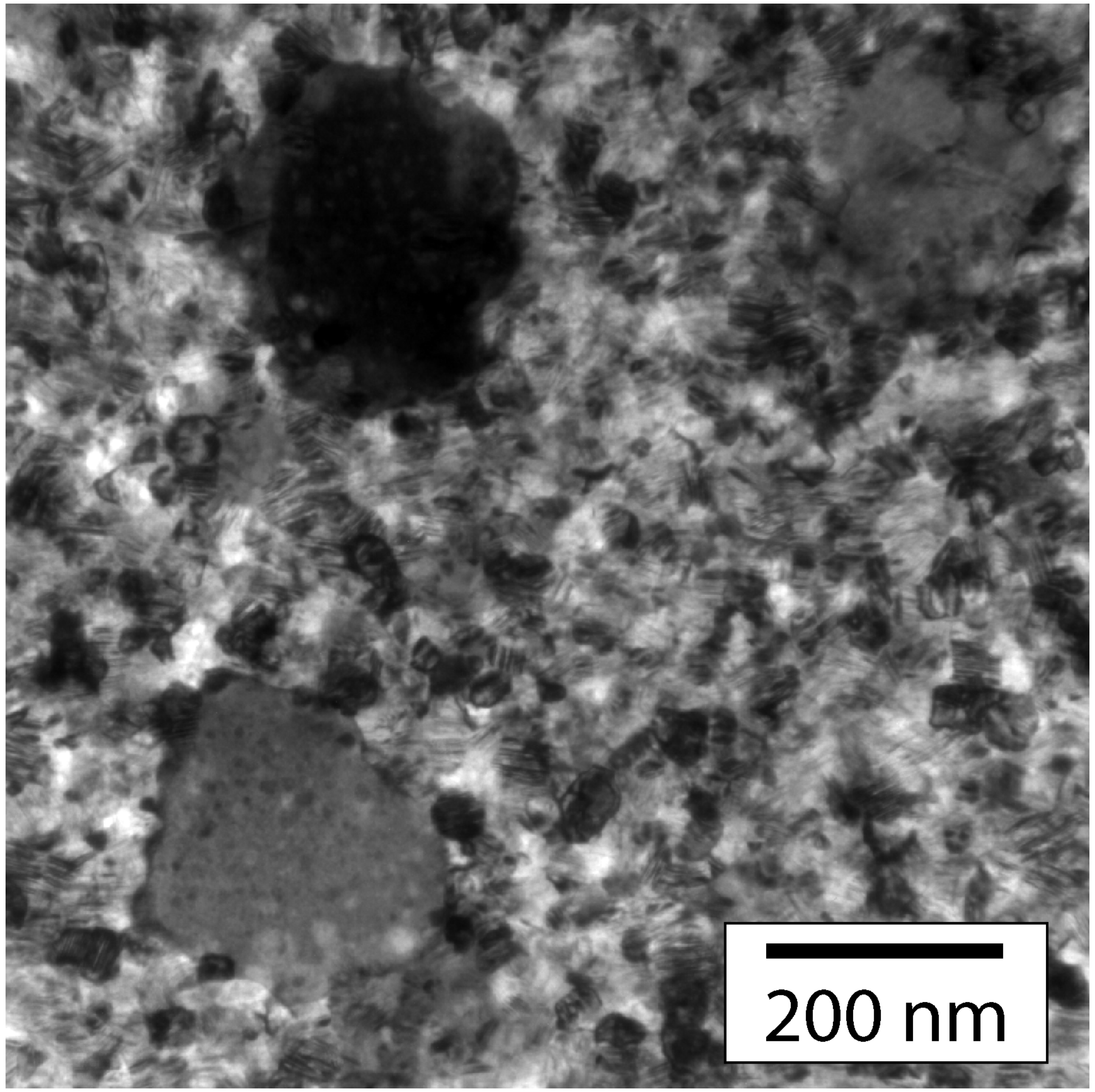
M.A. Atwater, K.A. Darling. ARL Tech Report ARL-TR-6007 2012.

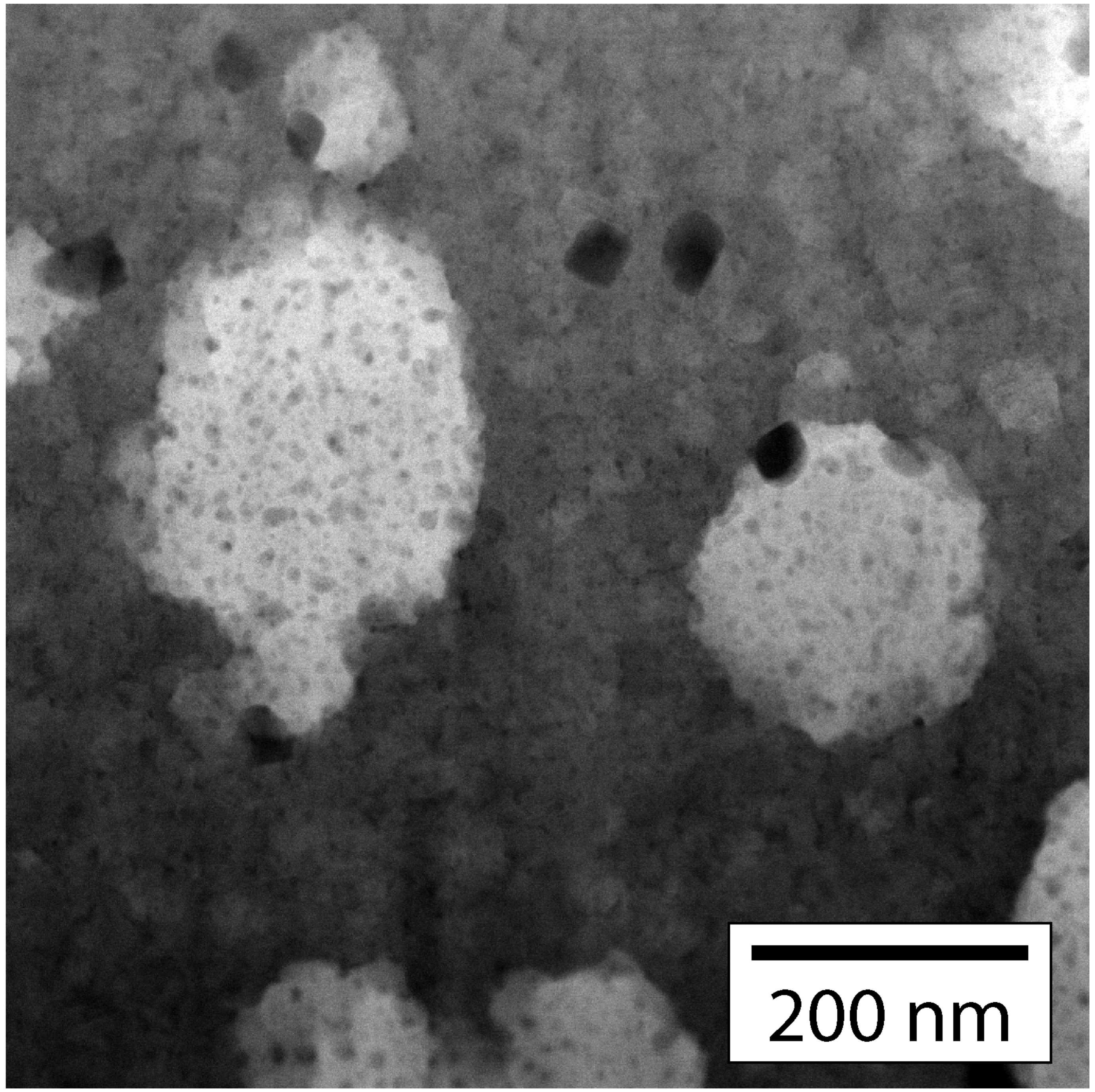
Ni-W Phase Diagram



Turchi PEA, Kaufman L, Liu ZK. Calphad Comput Coupling Phase Diagrams Thermochem 2006;30:70.

Electroplated Ni-W: Initial Analysis

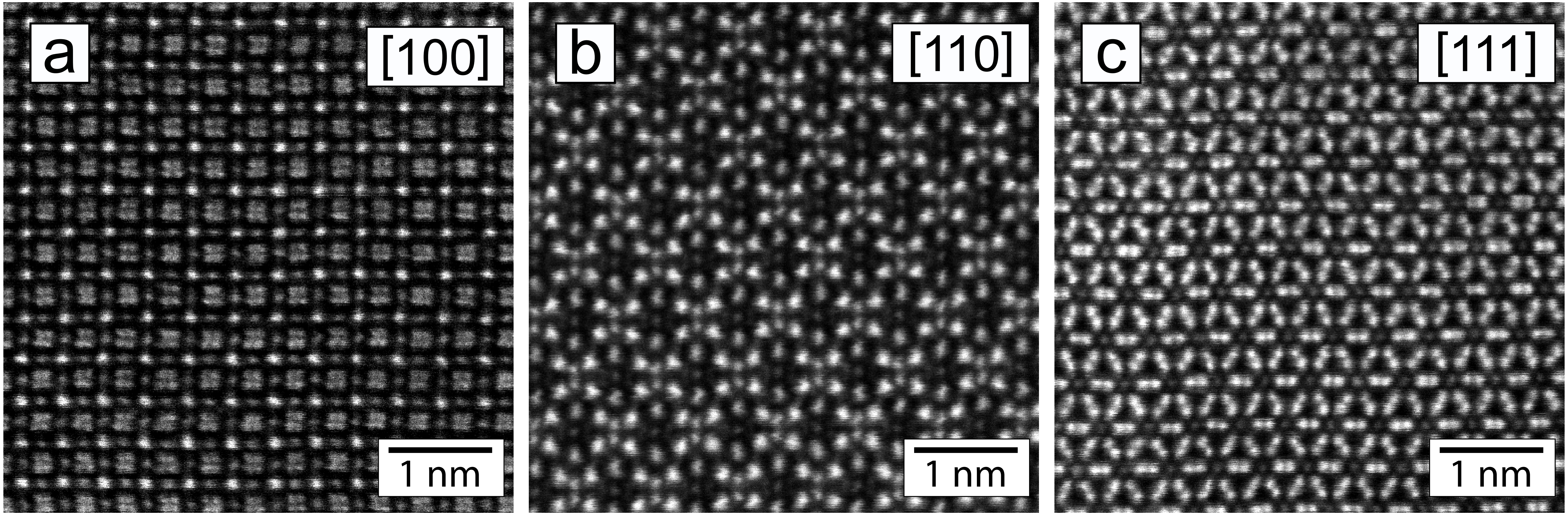




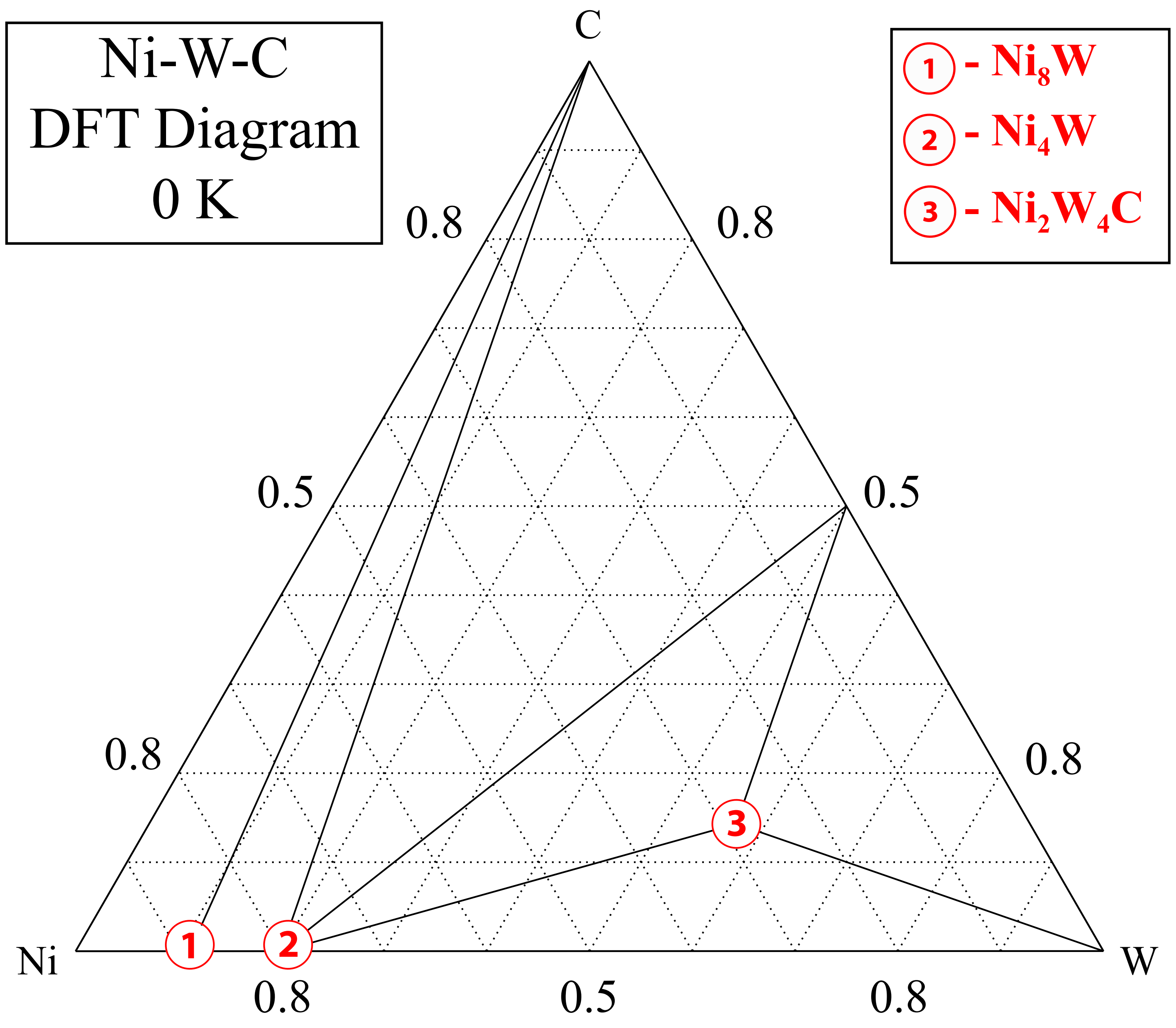
Several unknown phases → **Do not match phase diagram**

Bright phase is Ni_6W_6C

Ni_6W_6C is misidentified as intermetallic NiW

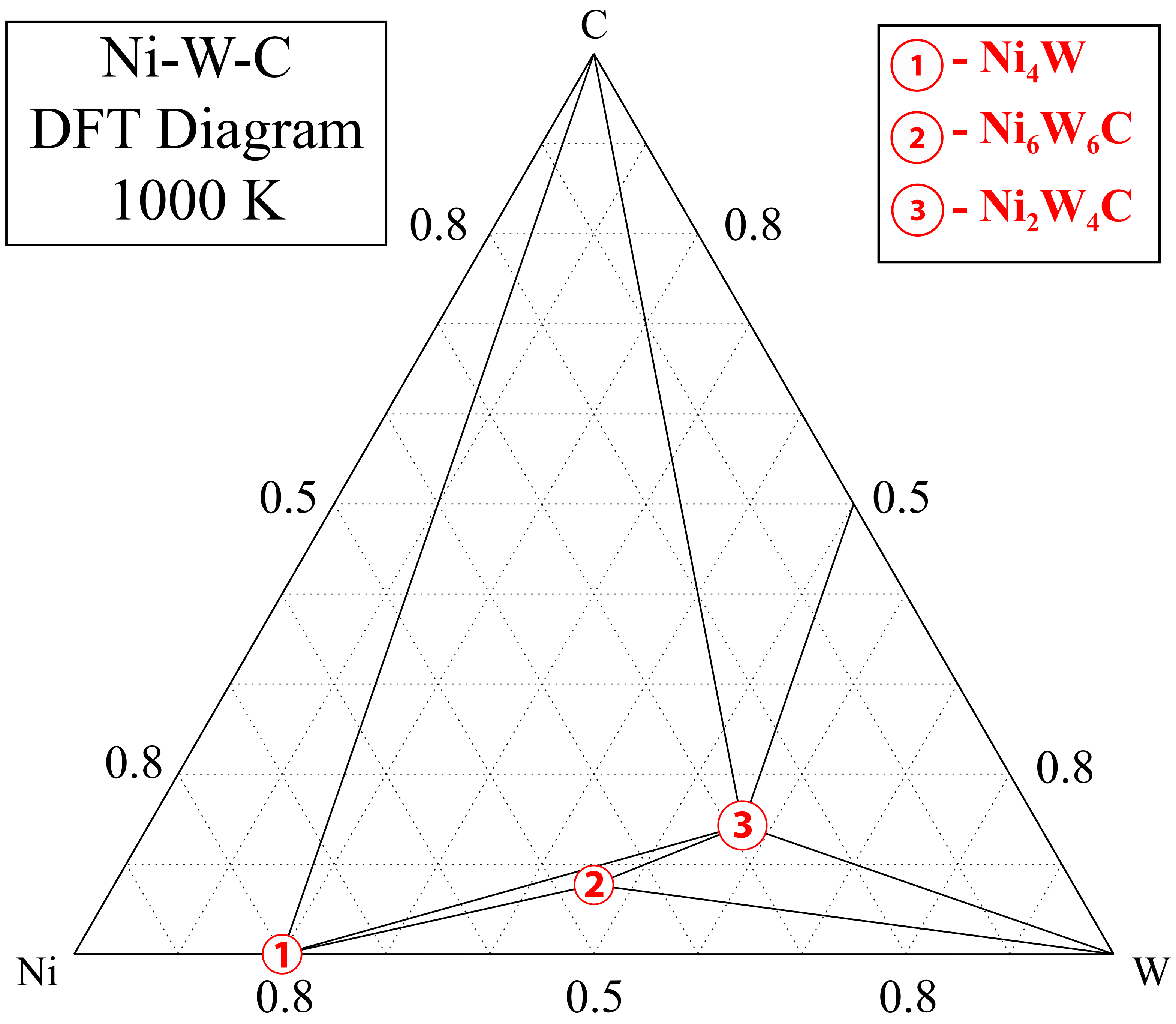


Ternary DFT phase diagrams



Ni-W-C
DFT Diagram
0 K

① - Ni_8W
② - Ni_4W
③ - Ni_2W_4C

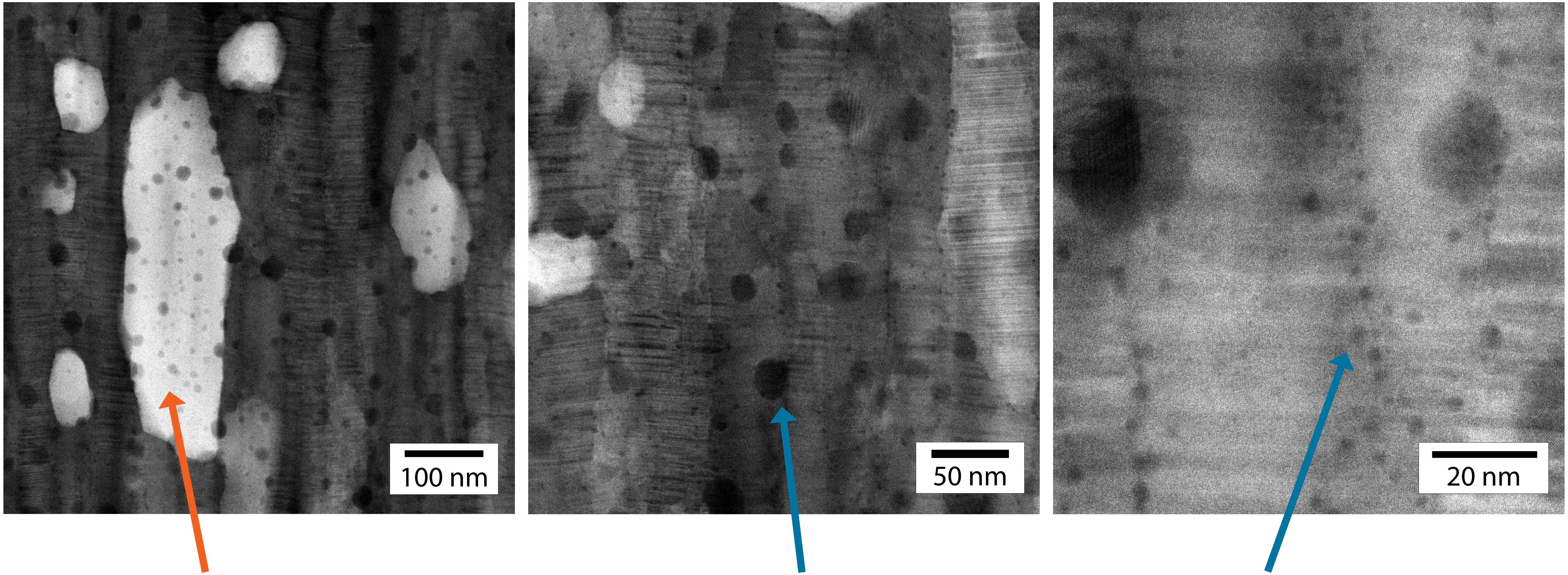


Ni-W-C
DFT Diagram
1000 K

① - Ni_4W
② - Ni_6W_6C
③ - Ni_2W_4C

Ni_6W_6C (and others) in sputtered films

Impurity phases may be more common than realized

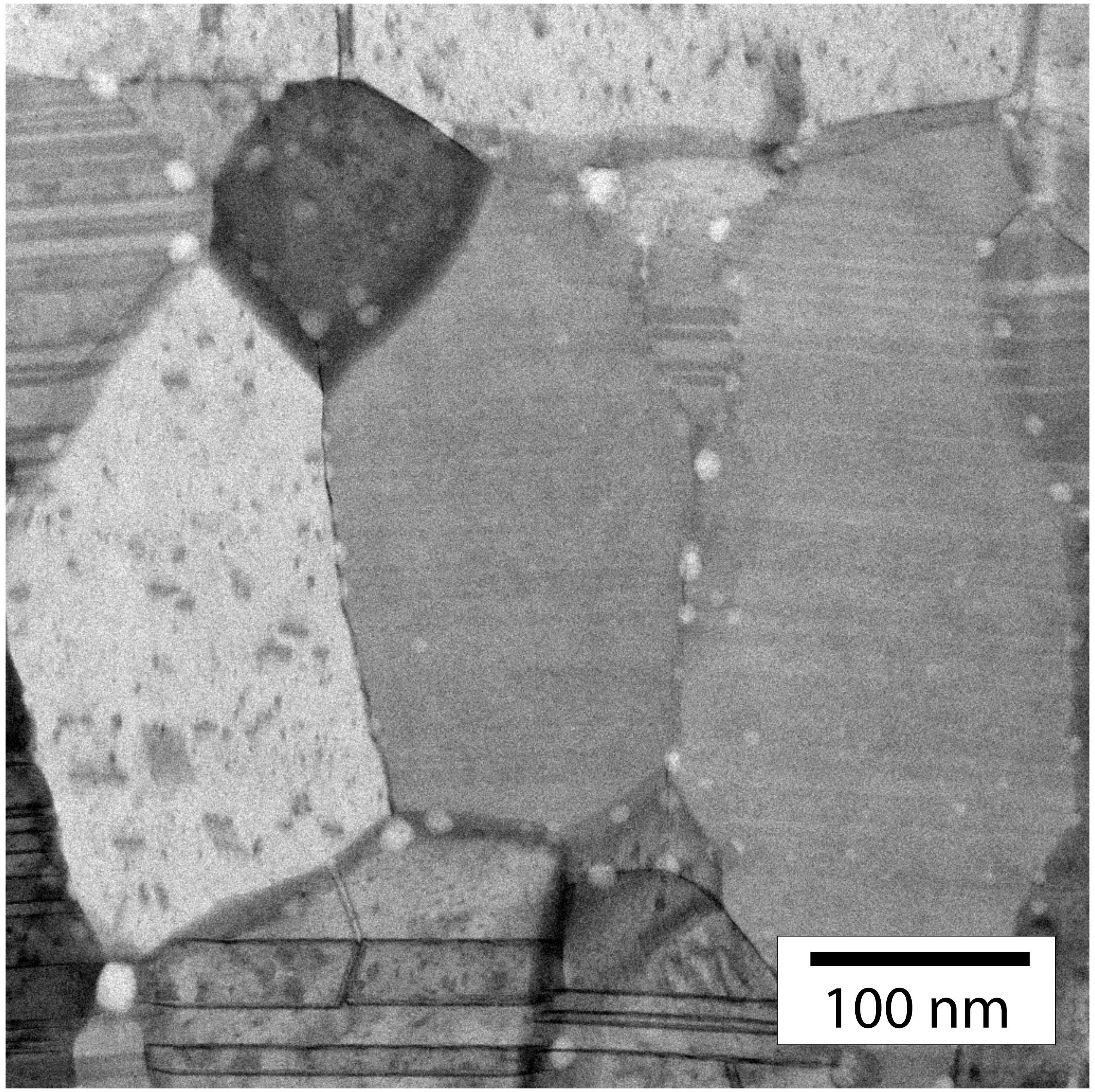


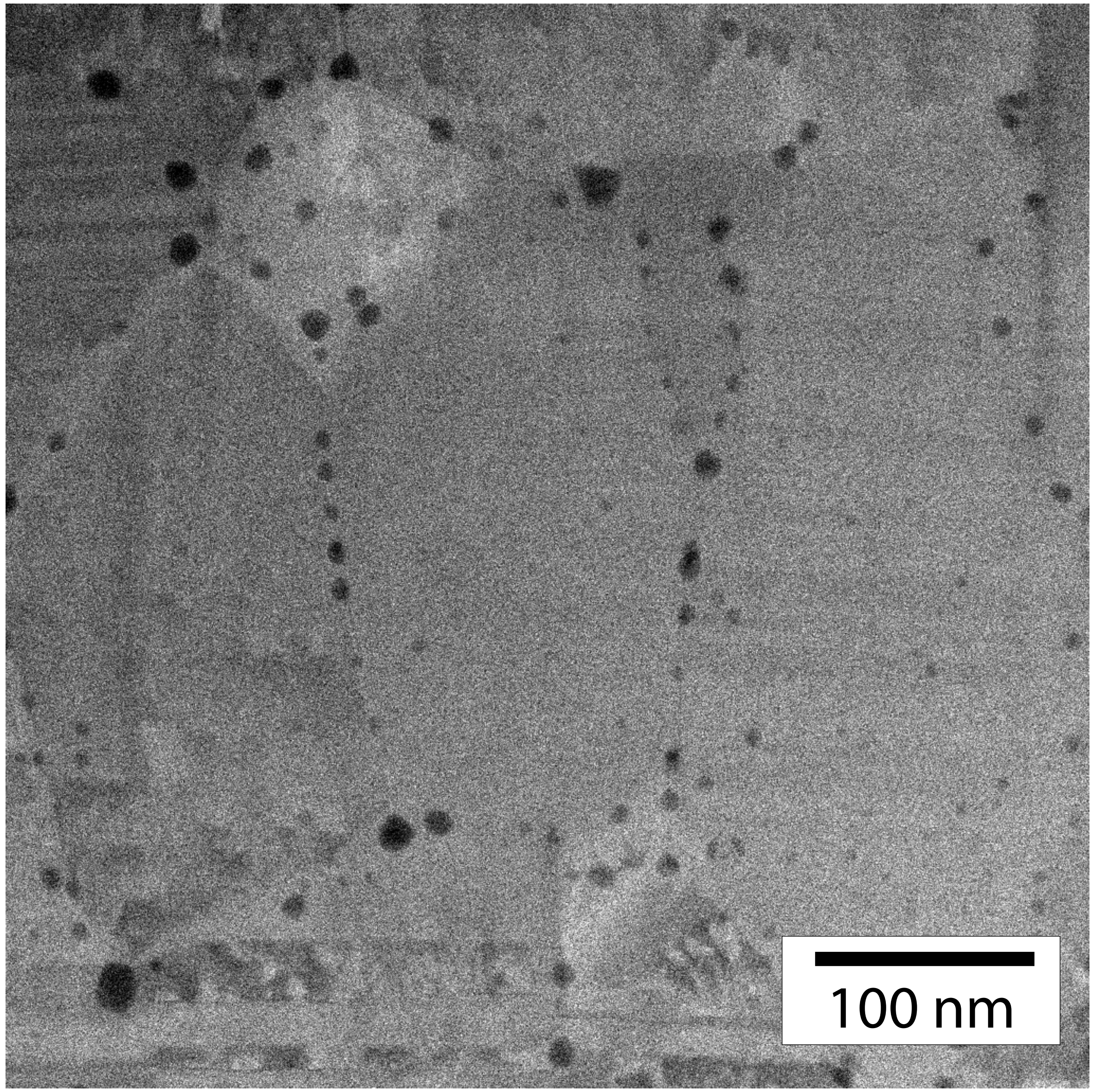
Carbide

Oxides & Large Ar Pores

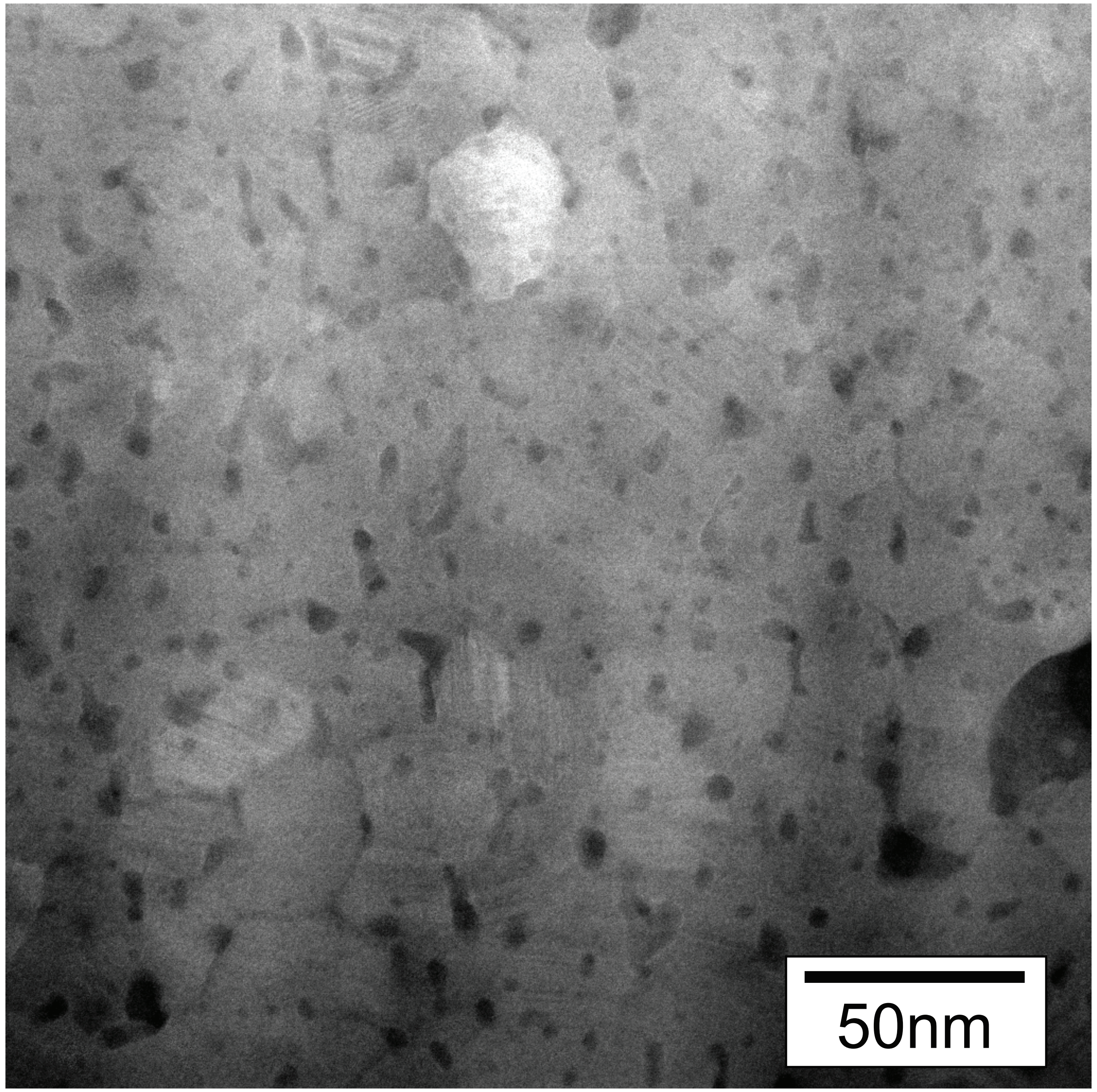
Small Ar Pores

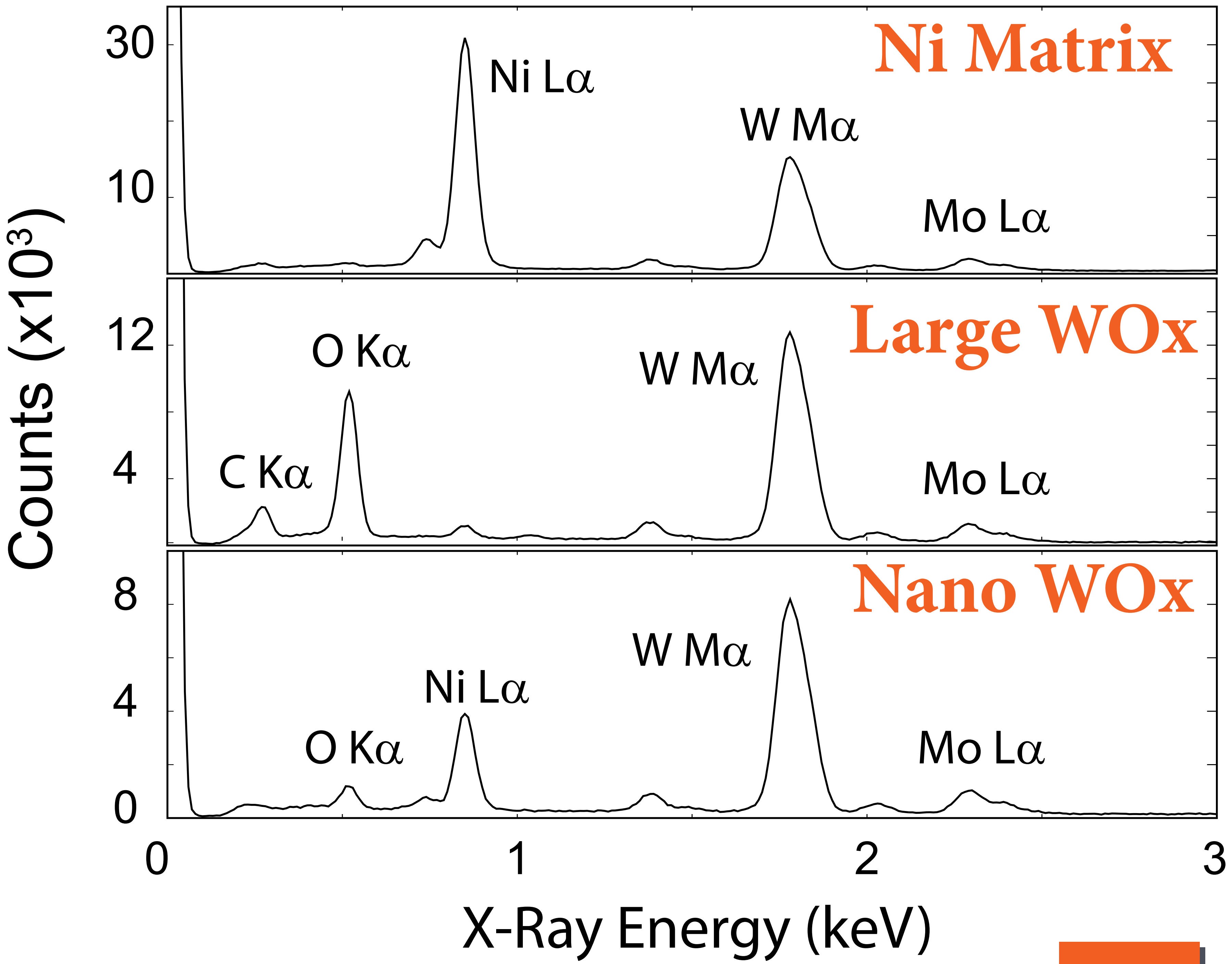
Ar pores pin grain growth?



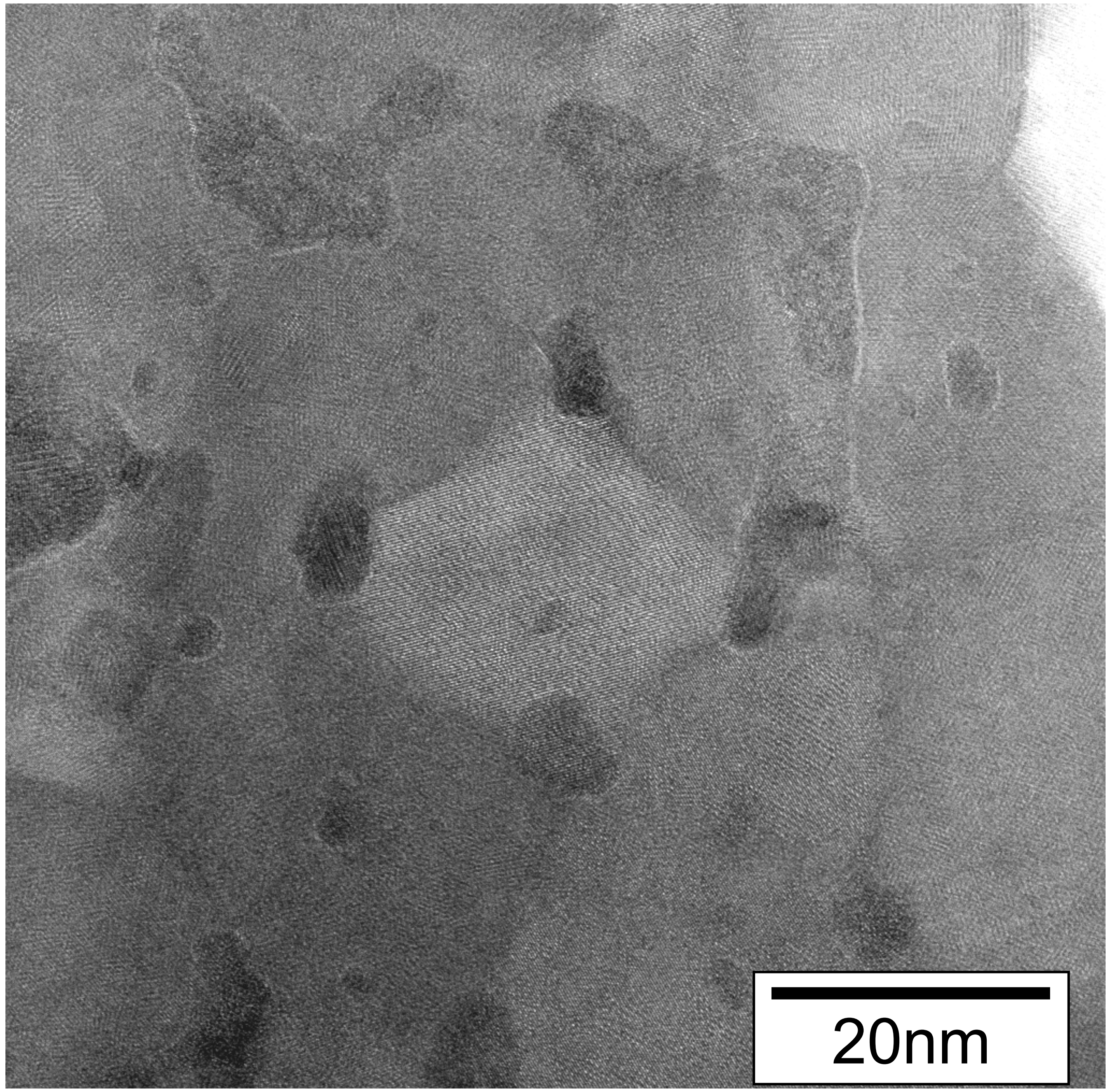


Dark phase is W-rich oxide





Nanoscale oxides pin grain growth?



Grain Radius ≈ 30 nm

Particle Radius ≈ 3 nm

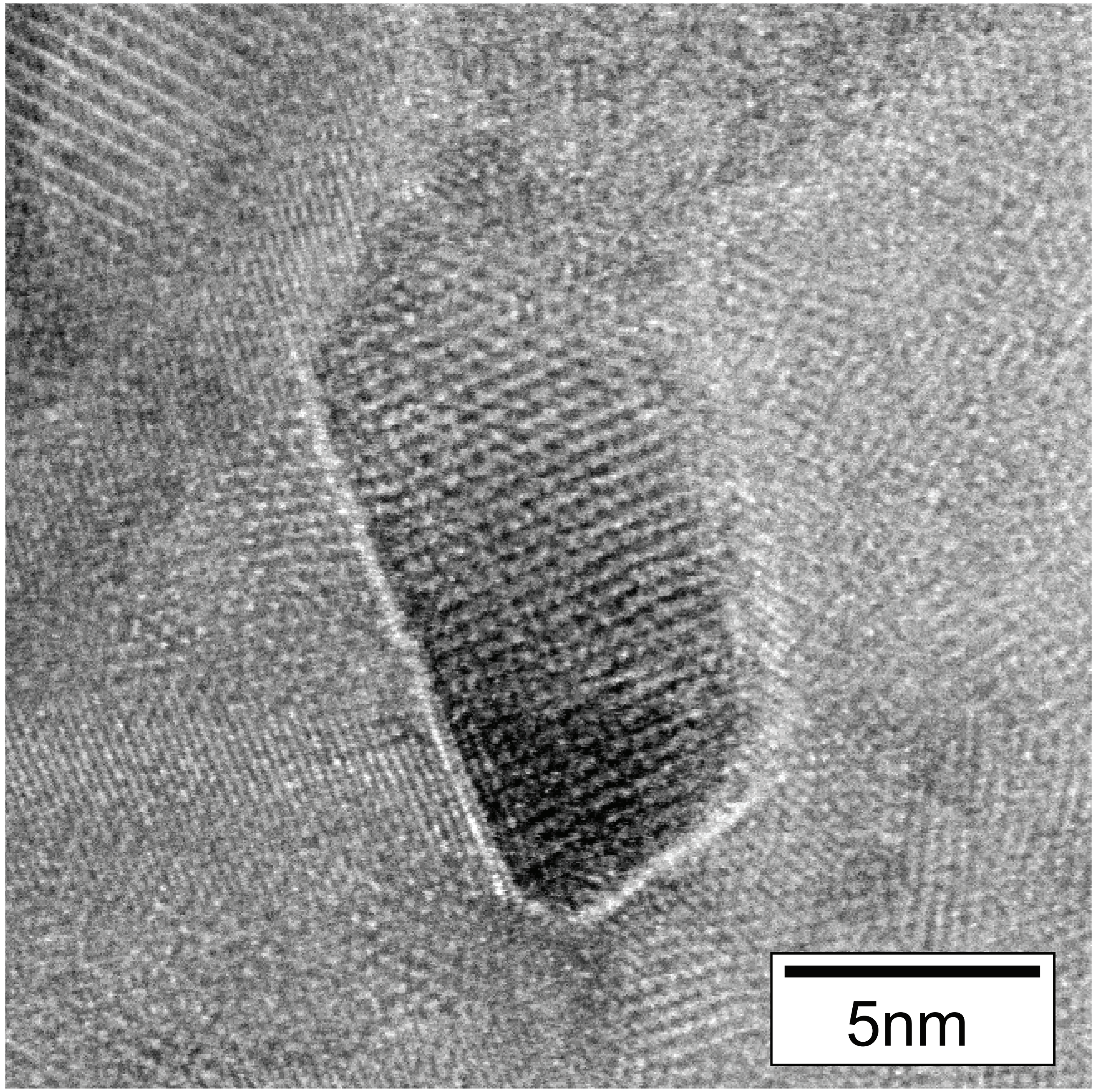
Measured Volume Fraction ≈ 3%

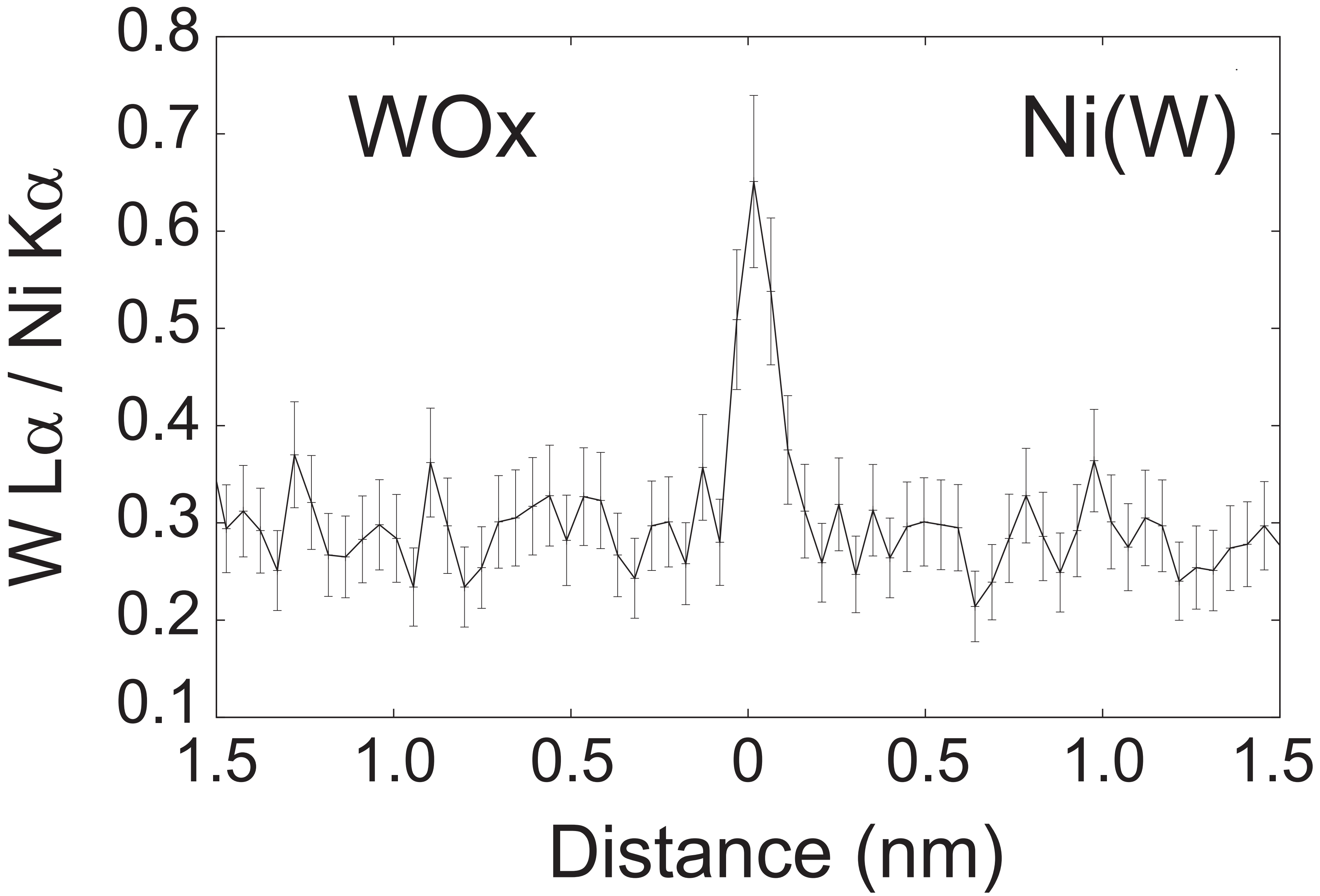
What volume fraction do we need?

$$f_{\mathrm{critical}} = \frac{r}{5R} = \frac{3\mathrm{nm}}{150\mathrm{nm}} = 2\%$$

R.D. Doherty, Mater. Sci. Forum 715-716 (2012) 1–12.

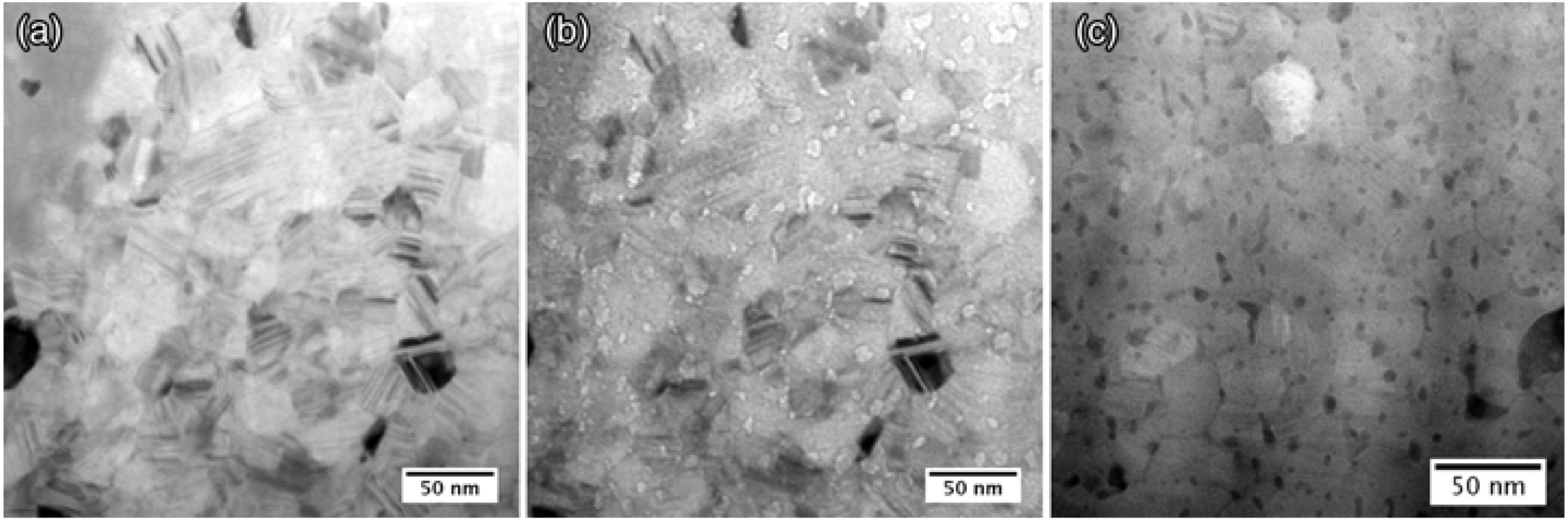
WOx Segregation





Finding the oxides

Focused TEM-BF **Underfocused TEM-BF** **STEM-HAADF**

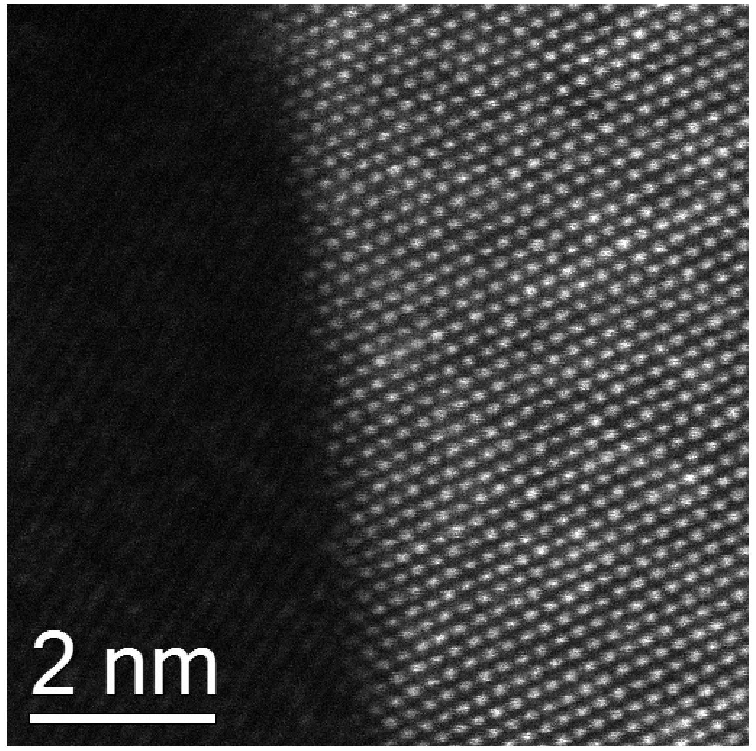


Search for W-segregation

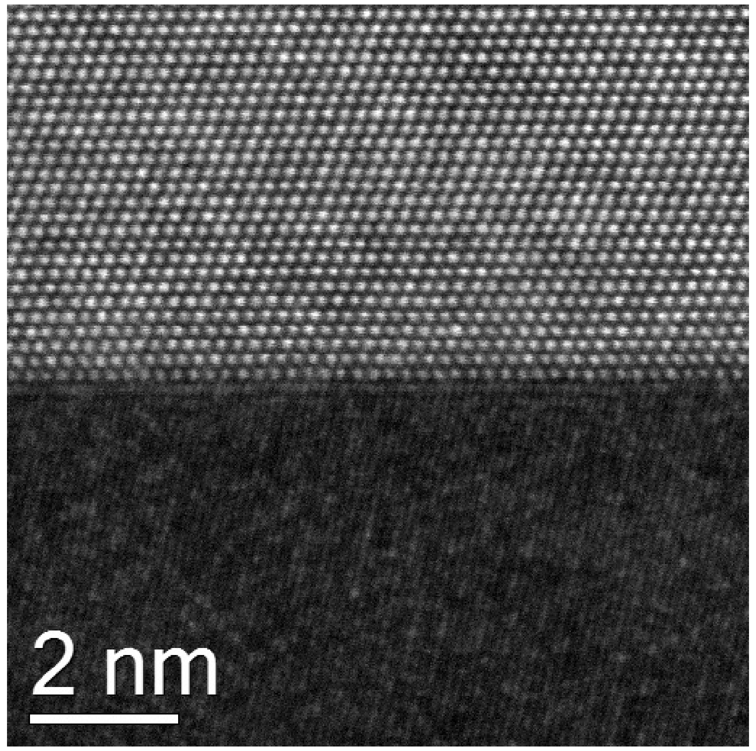
As-Deposited

700°C

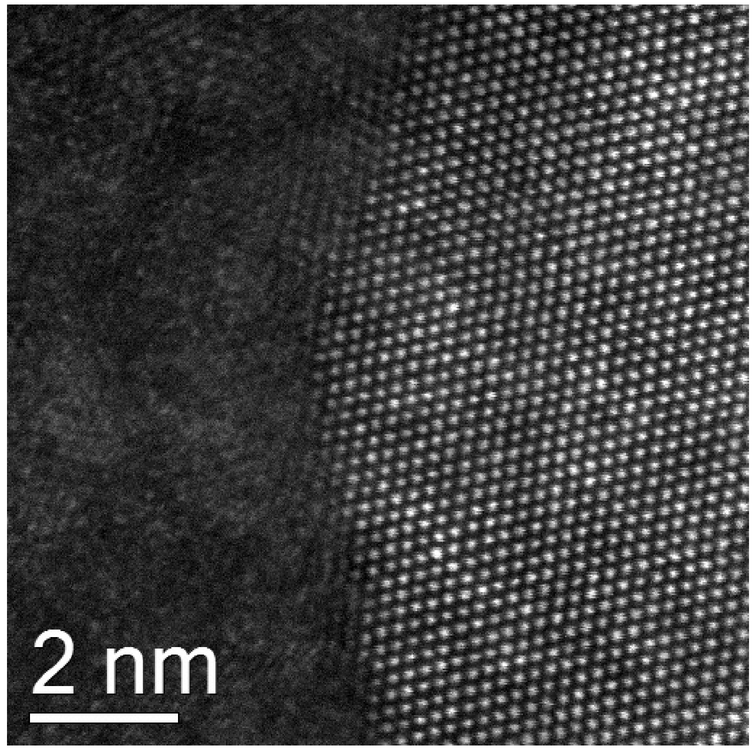
3at%



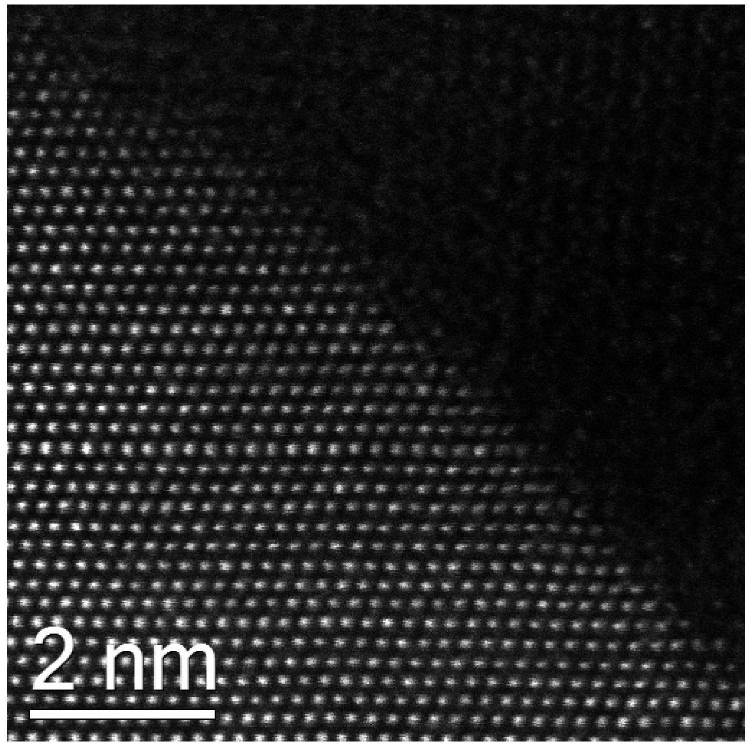
9at%



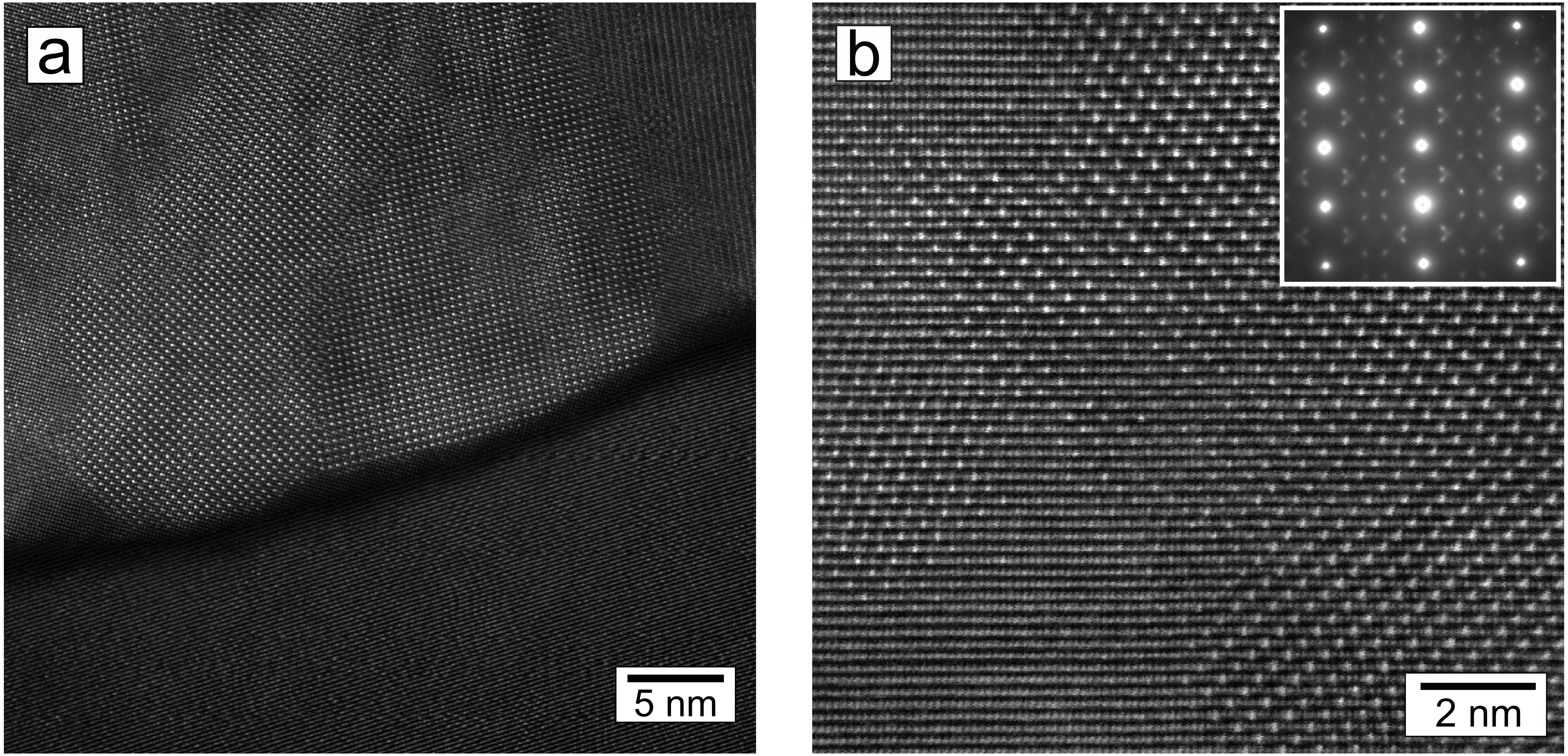
11at%



23at%



Ni_4W nucleate from W-rich boundaries?



A few open questions...

1. Is Ni-W an isolated example?
2. How pure is pure and do we care?
3. Can we dope nanograin materials with “impurities”?
4. Do we trust our computational models?
5. Are all nanocrystalline grain boundaries equal?
6. Can we truly characterize nanocrystalline microstructures?