

Mechanochemical synthesis of nanostructured metal nitrides, carbonitrides and carbon nitride: A combined theoretical and experimental study

Seyyed Amin Rounaghi^{1,*}, Danny E. P. Vanpoucke^{2,3}, Hossein Eshghi⁴, Sergio Scudino⁵,
Elaheh Esmaeili⁶, Steffen Oswald⁵, Jürgen Eckert^{7,8,**}

1) Department of Materials Engineering, Birjand University of Technology, 9719866981 Birjand,
Iran

2) UHasselt, Institute for Materials Research (IMO-IMOMEC), Agoralaan, 3590 Diepenbeek,
Belgium

3) IMOMEC, IMEC vzw, 3590 Diepenbeek, Belgium

4) Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, 91775-1436
Mashhad, Iran

5) Institute for Complex Materials, IFW Dresden, Helmholtzstraße 20, D-01069 Dresden, Germany

6) Department of Chemical Engineering, Birjand University of Technology, 9719866981 Birjand,
Iran

7) Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Jahnstraße 12, A-8700
Leoben, Austria

8) Department Materials Physics, Montanuniversität Leoben, Jahnstraße 12, A-8700 Leoben, Austria

*) Corresponding author. E-mail address: rounaghi@birjandut.ac.ir

**) Corresponding author. E-mail address: juergen.eckert@unileoben.ac.at

1. DFT calculations

Table S1. Crystallographic information and details of DFT calculations.

System	Symmetry	#Metal	#N	#C	KPT relax	KPT static	MaxForce/meV/Å
Aluminum							
Al	Fm-3m	4	0	0	15x15x15	21x21x21	0.00
Al:N Sub	2x2x2	31	1	0	9x9x9	13x13x13	0.25
Al:N Int T		32	1	0	5x5x5		2.05
Al:N Int O		32	1	0	5x5x5		2.06
Al:C Sub		31	0	1	9x9x9		0.52
Al:C Int T		32	0	1	5x5x5		0.48
Al:C Int O		32	0	1	5x5x5		1.10
AlN		P6 ₃ mc	2	2	0		15x15x15
AlN:C Sub	3x3x2	36	35	1	3x3x3	11x11x11	0.29
AlN:C Int H		36	36	1			1.84
AlN:C Int T		36	36	1			0.85
Al ₄ C ₃	R-3m	12	0	9	15x15x3	21x21x5	0.19
Al ₄ C ₃ :N Sub T	2x2x1	48	1	35	9x9x3	9x9x3	11.09
Al ₄ C ₃ :N Sub H		48	1	35	9x9x3	13x13x5	0.34
Al ₄ C ₃ :N Int H		48	1	36			0.46
Al ₄ C ₃ :N Int C		48	1	36			3.51
Titanium							
Ti	P6 ₃ /mmc	2	0	0	15x15x15	21x21x21	0.00
Ti:N Sub	3x3x2	35	1	0	5x5x5	9x9x9	0.28
Ti:N Int H		36	1	0			0.46
Ti:N Int C		36	1	0			0.13
Ti:C Sub		35	0	1			0.20
Ti:C Int H		36	0	1			0.15
Ti:C Int cage		36	0	1			0.29
TiN	Fm-3m	4	4	0	15x15x15	21x21x21	0.00
TiN:C Sub	2x2x2	32	31	1	5x5x5	13x13x13	0.06
TiN:C Int		32	32	1			0.07
TiC	Fm-3m	4	0	4	15x15x15	21x21x21	0.00
TiC:N Sub	2x2x2	32	1	31	5x5x5	13x13x13	0.12
TiC:N Int		32	1	32			0.19
Vanadium							
V	Im-3m	2	0	0	15x15x15	21x21x21	0.00
V:N Sub	3x3x3	53	1	0	5x5x5	13x13x13	0.11
V:N Int		54	1	0			0.95
V:C Sub		53	0	1			0.47
V:C Int		54	0	1			0.63
VN	Fm-3m	4	4	0	15x15x15	21x21x21	0.00
VN:C Sub	2x2x2	32	31	1	5x5x5	13x13x13	0.15
VN:C Int		32	32	1			0.30
V ₂ N	Pbcn	8	4	0	15x15x15	21x21x21	0.22
V ₂ N:C Sub	2x2x2	64	31	1	5x5x5	11x11x11	0.15
V ₂ N:C Int		64	32	1			0.22
VC	Fm-3m	4	0	4	15x15x15	21x21x21	0.00
VC:N Sub	2x2x2	32	1	31	5x5x5	13x13x13	0.08
VC:N Int		32	1	32			0.24

Chromium							
Cr	Im-3m	2	0	0	15x15x15	21x21x21	0.00
Cr:N Sub	3x3x3	53	1	0	5x5x5	13x13x13	0.11
Cr:N Int		54	1	0			0.22
Cr:C Sub		53	0	1			0.37
Cr:C Int		54	0	1			0.34
CrN	Fm-3m	4	4	0	15x15x15	21x21x21	0.00
CrN:C Sub	2x2x2	32	31	1	5x5x5	13x13x13	0.07
CrN:C Int		32	32	1			0.41
CrC	Fm-3m	4	0	4	15x15x15	21x21x21	0.00
CrC:N Sub	2x2x2	32	1	31	5x5x5	13x13x13	0.23
CrC:N Int		32	1	32			0.32
Cr ₂₃ C ₆	Fm-3m	92	0	24	5x5x5	11x11x11	0.30
Cr ₂₃ C ₆ :N Sub	1x1x1	92	1	23	5x5x5	13x13x13	0.73
Cr ₂₃ C ₆ :N Int		92	1	24	5x5x5		0.12

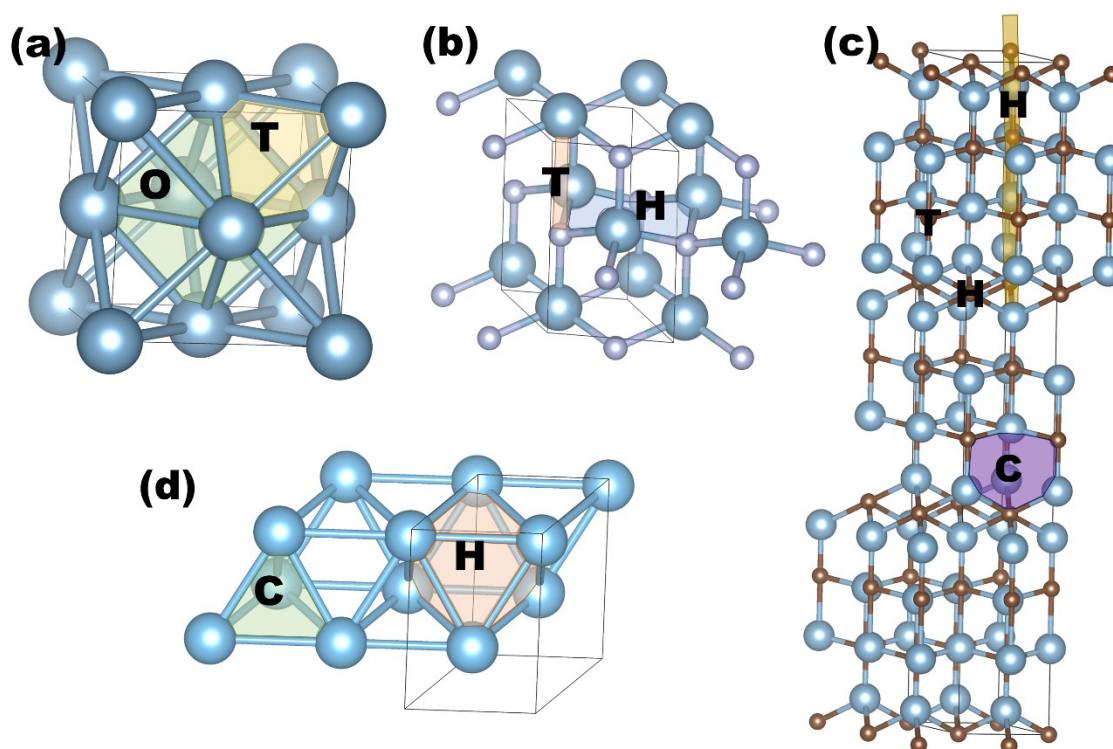


Figure S1: Ball-and-stick representation of the Al (a), AlN (b) Al₄C₃ (c) and Ti (d) atomic structure. Different interstitial sites are indicated, as well as the two possible substitutional sites in Al₄C₃.

2. XRD analysis

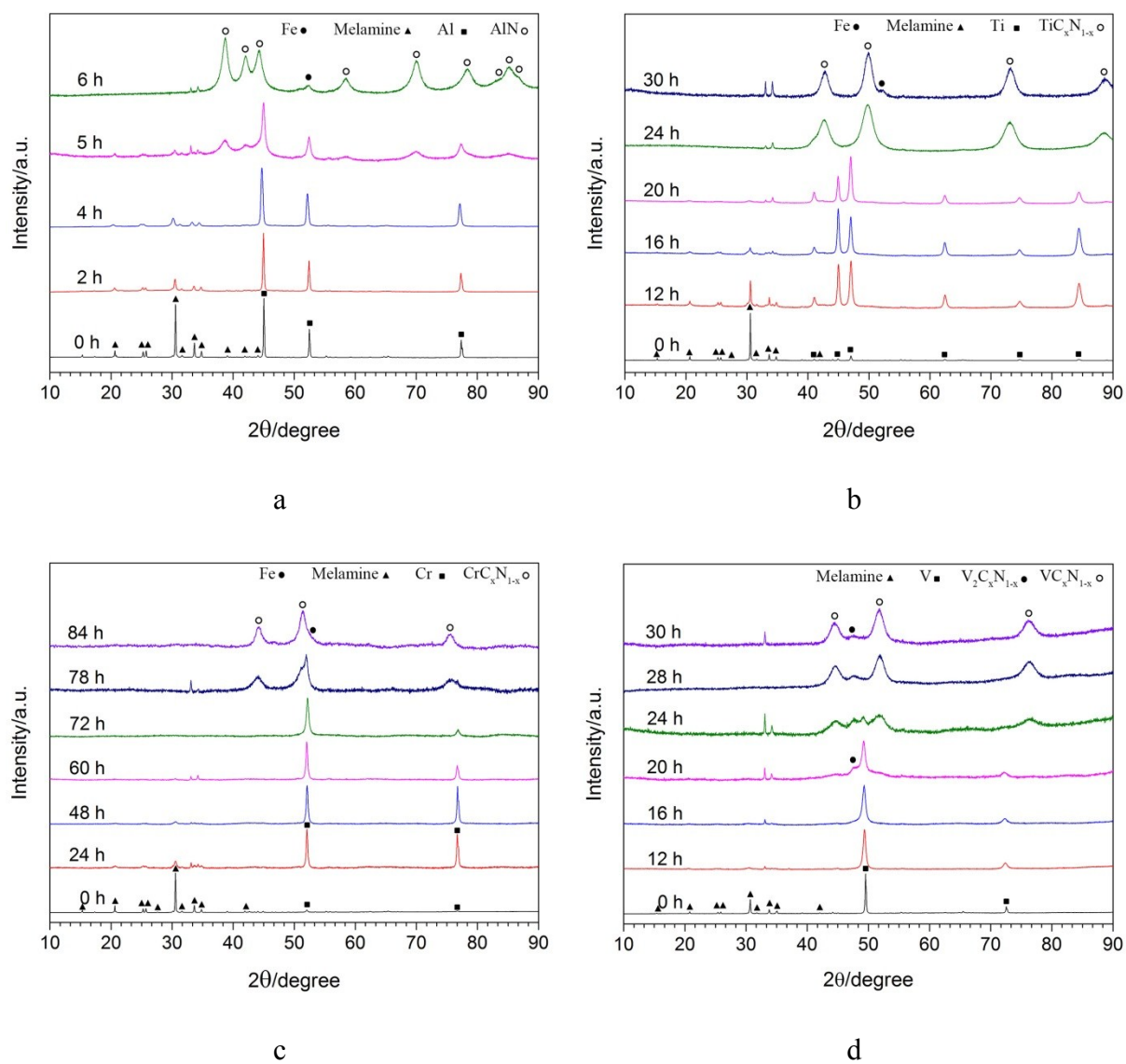


Figure S2. XRD patterns of a) Al-M, b) Ti-M, c) Cr-M and d) V-M powder mixtures milled for various milling times.

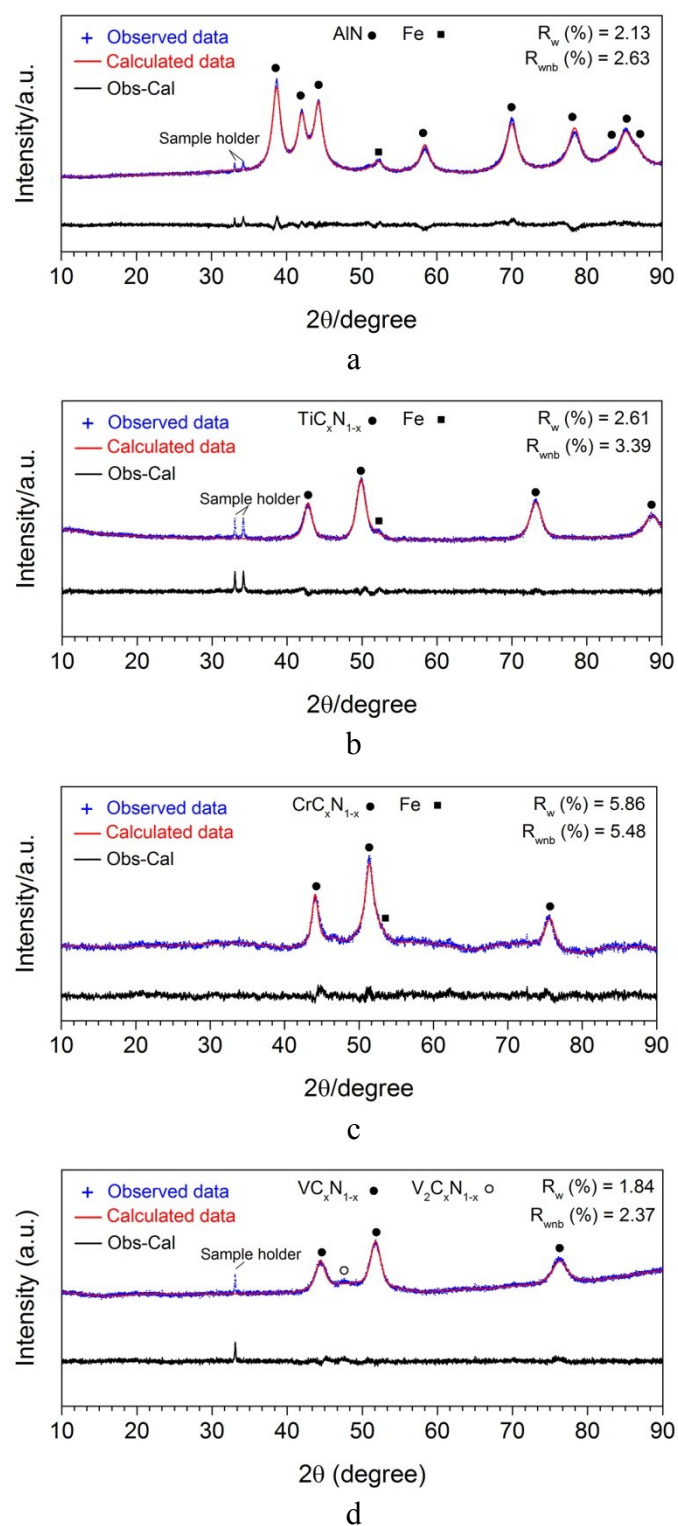
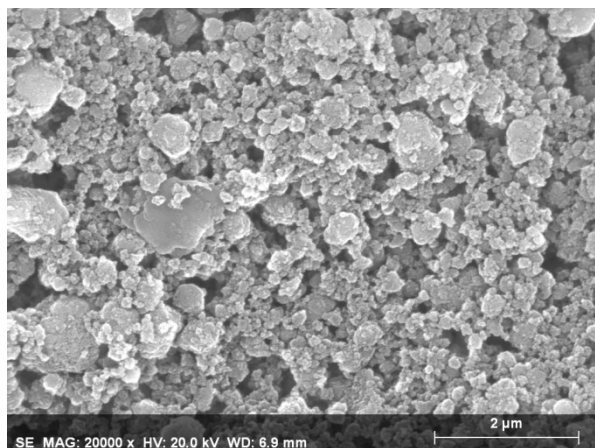
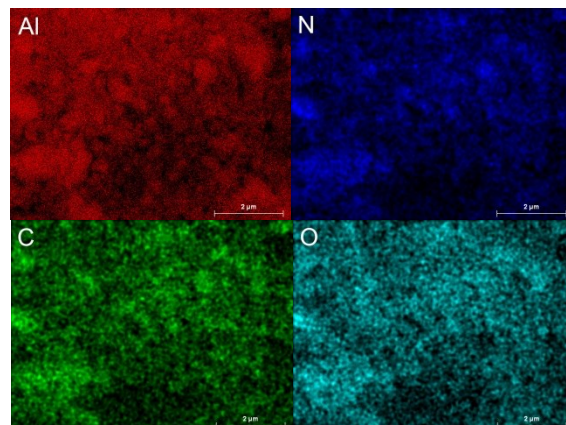


Figure S3. Observed and Calculated XRD profiles for a) Al-M, b) Ti-M, c) Cr-M and d) V-M powder mixtures milled for 6, 30, 84 and 30 h, respectively. The bottom black line is the difference between the observed and the calculated intensity (Obs-Cal).

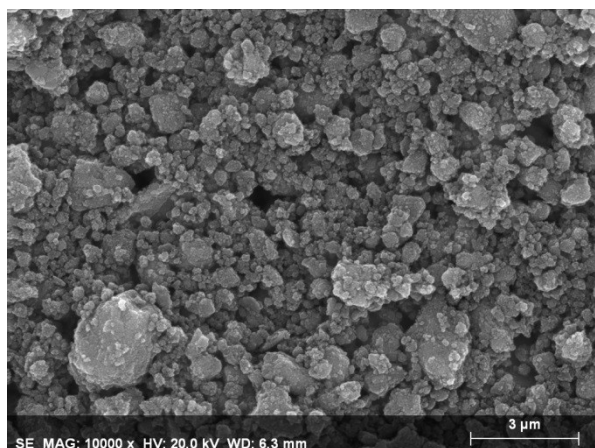
3. EDX analysis



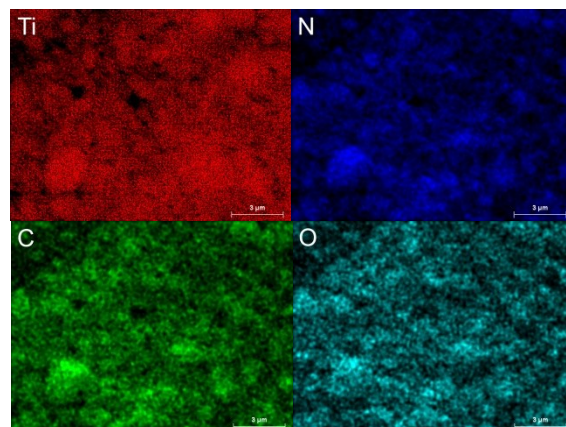
a



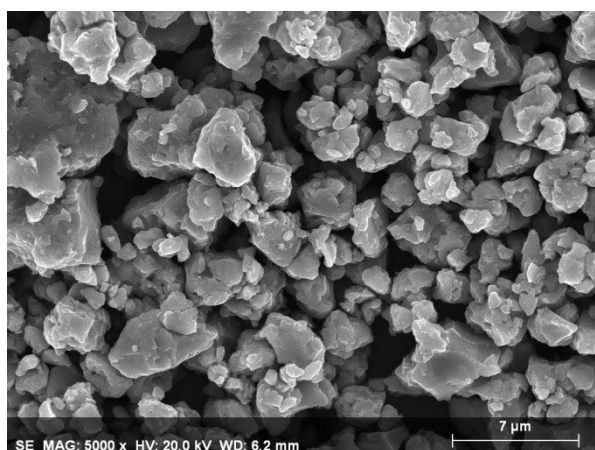
b



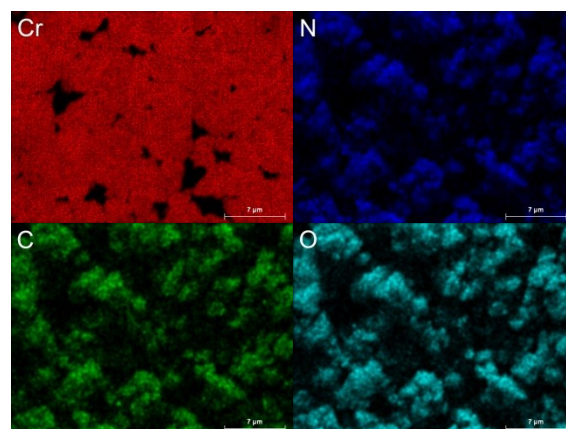
c



d



e



f

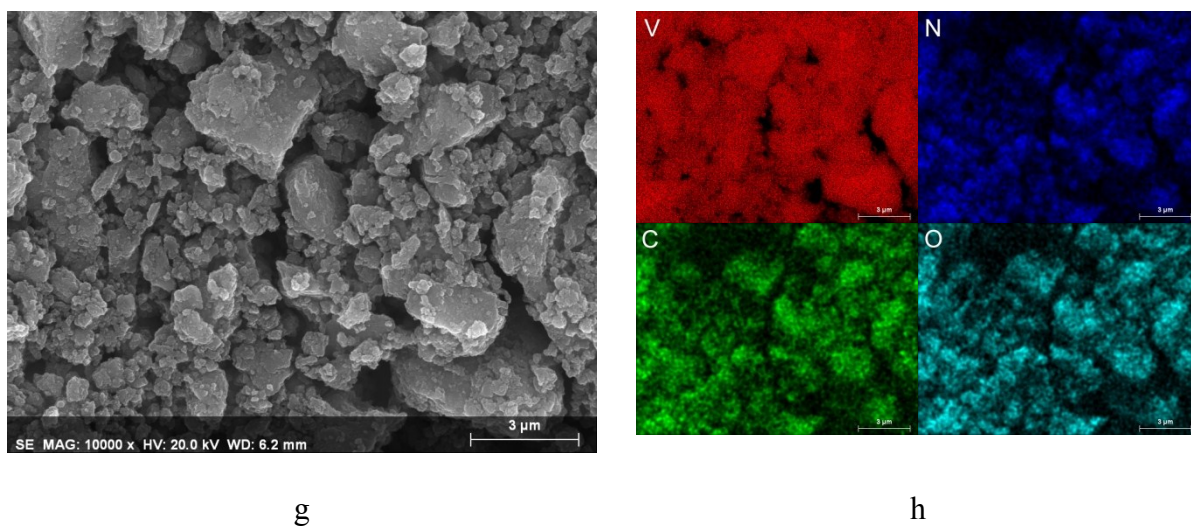


Figure S4. Typical SEM image with corresponding EDX mapping analysis obtained from a, b) Al-M, c, d) Ti-M, e, f) Cr-M and g, h) V-M powder mixtures milled for 6, 30, 84 and 30 h, respectively.