Thermal stability and dynamical properties of $Ti_3SiC_2(0001)$ at high temperatures: First-principles calculations

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www.gnm.cl

4th Workshop on novel methods for electronic structure calculations, and first southamerican congress on materials
Universidad Nacional de La Plata, Argentina

Research in Chile

Ranking Iberoamericano 2010	Universidad
1 (18)	Universidad de Chile
2 (32)	Pontificia Universidad Católica de Chile
3 (56)	Universidad de Concepción
4 (104)	Universidad de Santiago de Chile
5 (108)	Universidad Austral de Chile
6 (126)	
7 (137)	
8 (144)	
9 (156)	
10 (164)	

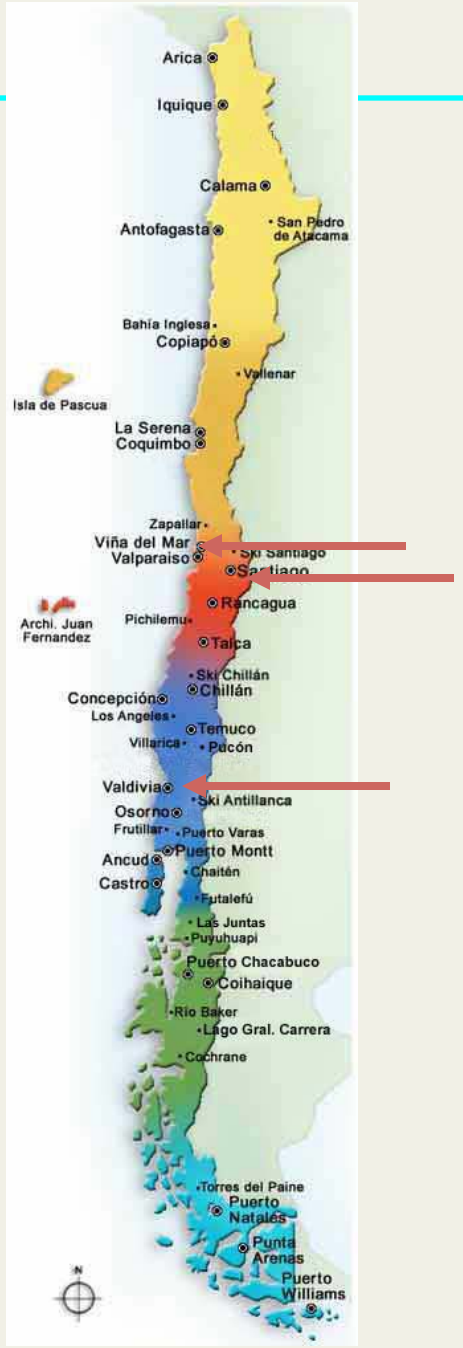
Population 15 millions

Santiago ~ 4 millions

Not good education…

+ 3-4 other places and
2-3 non-university institutes

Ab-initio in Chile



Approx 20-25 faculty + 10-12 PhD student

Santiago

Uchile 4+6

PUC: 4

USACH 3

UNAB 1+3

Valparaiso

UTFSM-PUCV: 2

Valdivia

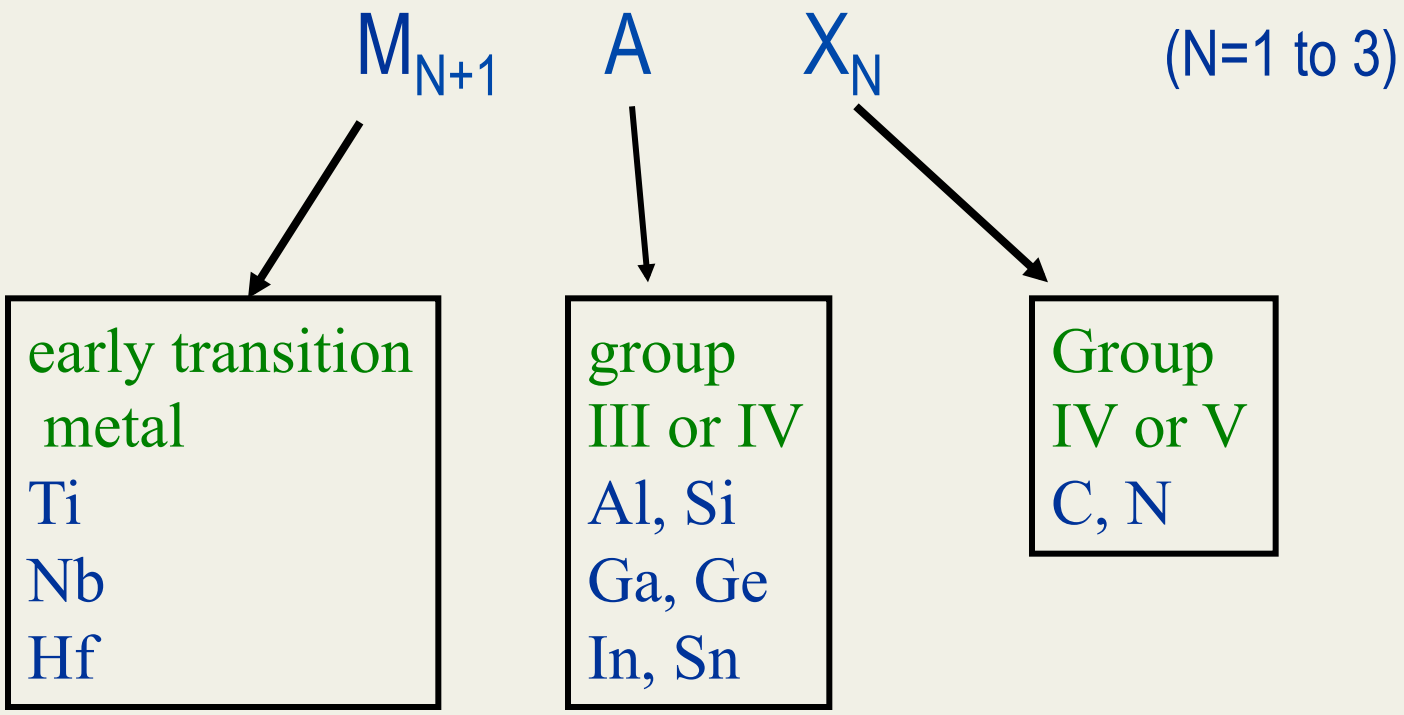
UACH: 3

Outline

- ✓ Introduction
- ✓ Theoretical approach
- ✓ Stability and energetics of $Ti_3SiC_2(0001)$ at 0K
- ✓ Stability of $Ti_3SiC_2(0001)$ at high temperature (up to 1400 °C)
- ✓ Oxidation processes by O_2 and H_2O
- ✓ Conclusions

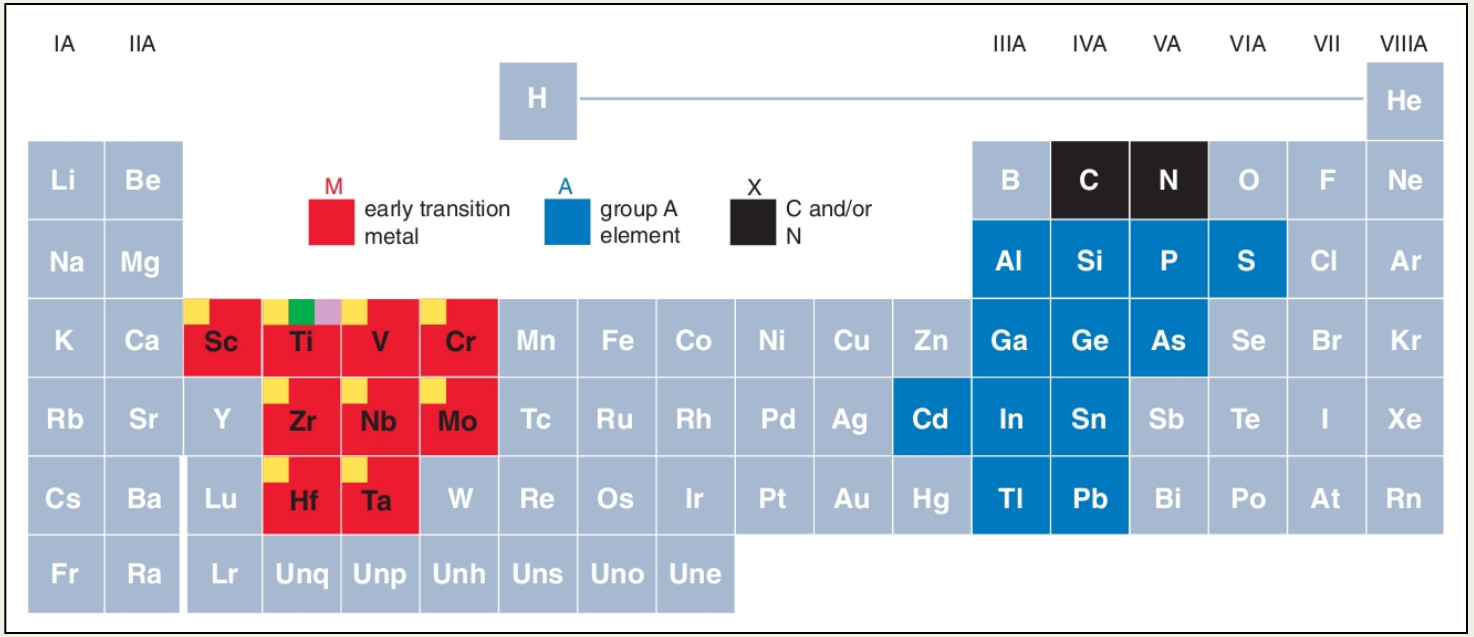
MAX Phases

Ternary layered compounds



Ex.: Ti_2AlC, Ti_3SiC_2 , Ti_4AlN_3

MAX Phases



-1967:
Synthesized by Nowotny et al.
-1990':
study by Barsoum et al.

-More than 60 Max phases has been obtained to date

211

Ti_2AlC*	Ti_2AlN*	Hf_2PbC*	Cr_2GaC	V_2AsC	Ti_2InN
Nb_2AlC*	$(Nb,Ti)_2AlC$*	$Ti_2AlN_{0.5}C_{0.5}$*	Nb_2GaC	Nb_2AsC	Zr_2InN
Ti_2GeC*	Cr_2AlC	Zr_2SC	Mo_2GaC	Ti_2CdC	Hf_2InN
Zr_2SnC*	Ta_2AlC	Ti_2SC	Ta_2GaC*	Sc_2InC	Hf_2SnN
Hf_2SnC*	V_2AlC	Nb_2SC	Ti_2GaN	Ti_2InC	Ti_2TlC
Ti_2SnC*	V_2PC	Hf_2SC	Cr_2GaN	Zr_2InC	Zr_2TlC
Nb_2SnC*	Nb_2PC	Ti_2GaC	V_2GaN	Nb_2InC	Hf_2TlC
Zr_2PbC*	Ti_2PbC*	V_2GaC	V_2GeC	Hf_2InC	Zr_2TlN

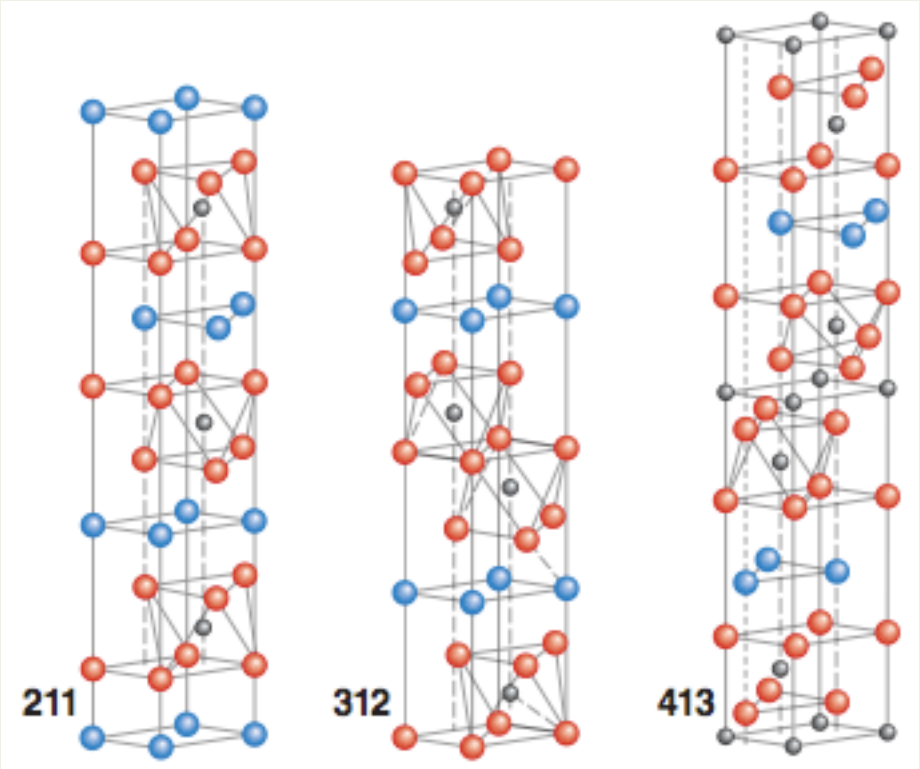
312

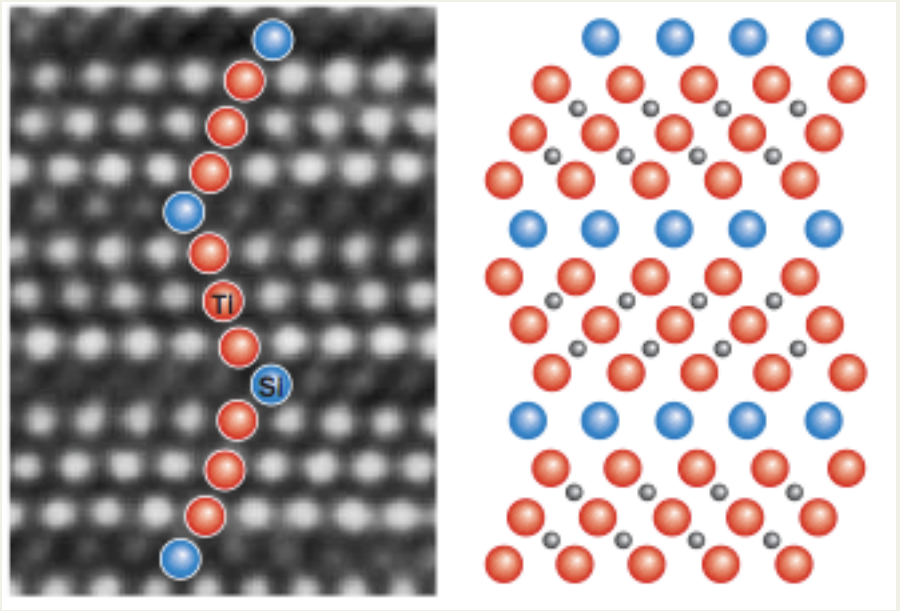
Ti_3AlC_2* Ti_3GeC_2*
Ti_3SiC_2*

413

Ti_4AlN_3*

MAX Phases: structure





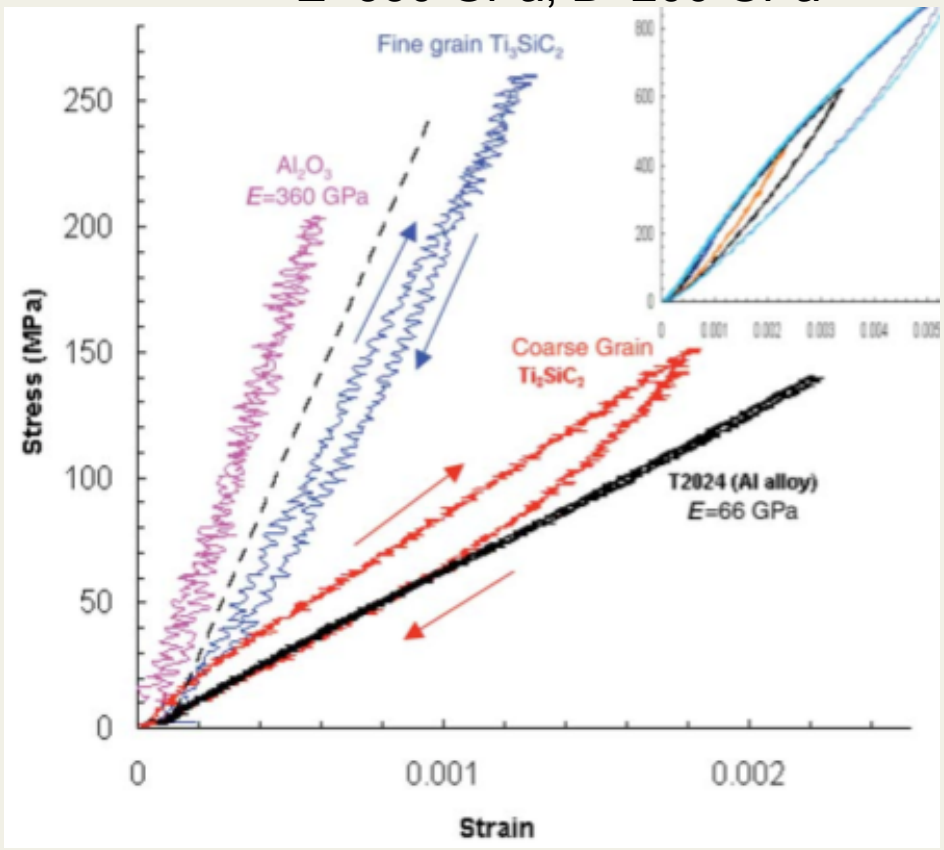
Ti_2AlC Ti_3SiC_2 Ti_4AlN_3

(Micrograph by L .Farber & I. Levin, NIST)

Max Phases: properties

Best attributes of metals and ceramics

E=330 GPa, B=206 GPa



Like metals:

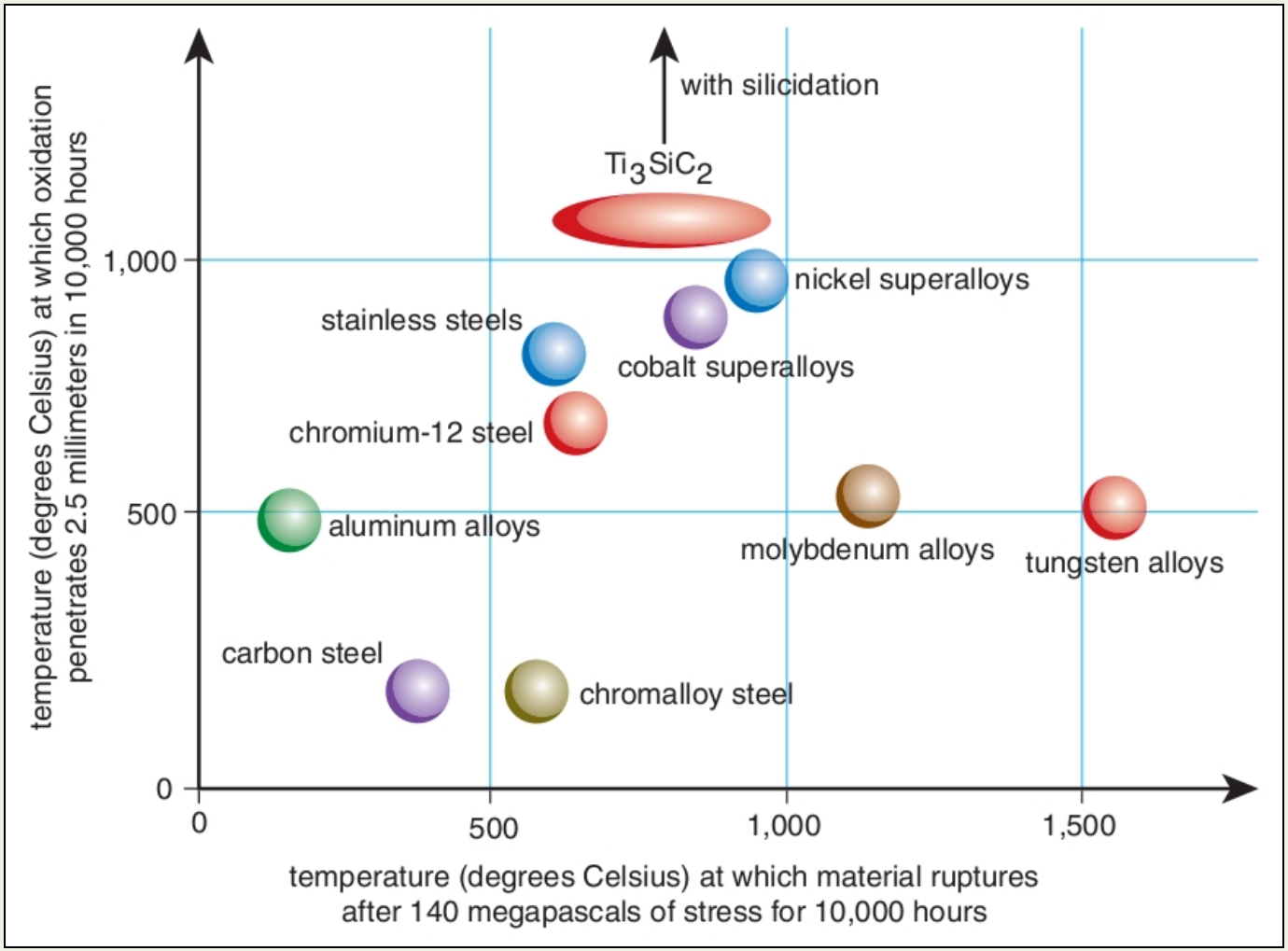
-Thermal and electrical conductors (better than Ti)
-Readily machinable
-Plastic at high temperatures

Like ceramics:

-Elastically rigid
-Lightweight
-Maintain their strengths at high temperature

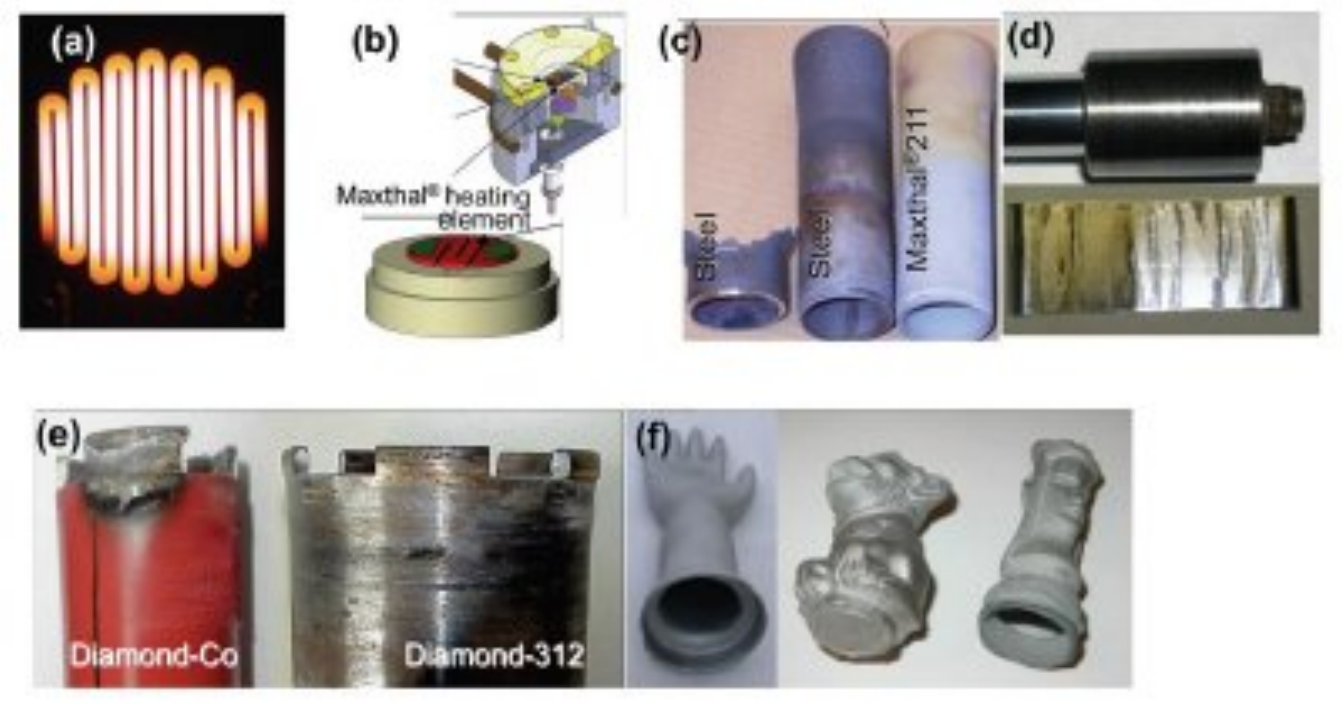
Barsoum (2001)

Oxidation v/s rupture with temperature



M. W. Barsoum & T. El-Raghy, American Scientist 89, 334 (2001)

MAX phases: applications



(From Kanthal Corp. Sweden, and 3-ONE- 2 Company)

a) and b): heating elements
c) gas burner nozzles in corrosive environments,
d) high-temperature bearings,
e) diamond/Ti3SiC2 composites for dry drilling of concrete (developed with Hilti Corp.),
f) examples of very thin walled parts manufactured by slip casting.

MAX phases: stiff, lightweight and ductile

Potential applications in high-performance jet engines for aircraft

The current jet engine technology (TiNi and TiAl alloys, like those used in the Airbus A330), is limited by material failure at high temperatures.

$Ti_3SiC_2(0001)$

- ✓ Ti_3SiC_2 is a representative member of $M_{n+1}AX_n$ class of materials
- ✓ It shows remarkable combination of properties between metal and ceramic with resistance to chemical attack (oxidation and corrosion) suggesting application as coating materials.
- ✓ Experiments show than Ti_3SiC_2 thin films are stable during vacuum furnace up to 1100-1200 °C, above which a decomposition is initiated by out-diffusion and evaporation of Si atoms from the top of (0001) surface on a nanometer depth scale.
  Emmerlich *et al*., Acta Materialia 55, 1497 (2007)
- ✓ The thermophysical and corrosion-resistant properties of $Ti_3SiC_2(0001)$ in the atomic scale are currently unknown

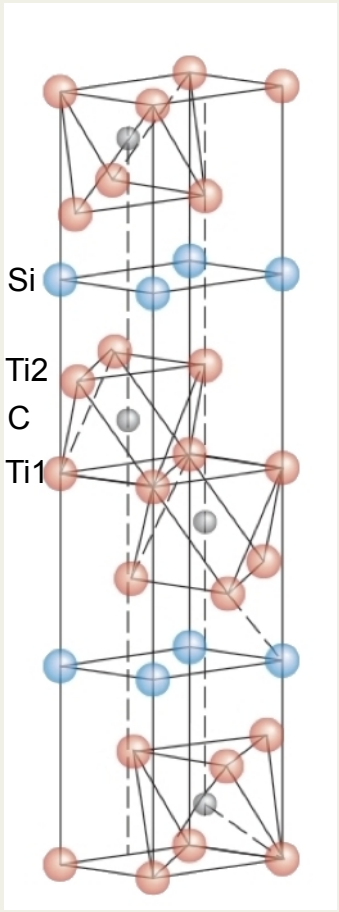
What we have done*

- ✓ Determine the energetic and electronic properties for all $Ti_3SiC_2(0001)$ surface terminations (at 0K).
  - ✓ Density functional theory calculations (DFT-GGA), SIESTA code.
  - ✓ Symetrical slab of (3x3) surface unit cell (19-23 Monolayers).
  - ✓ Brillouin zone sampling: 3x3x1 Monkhorst-Pack mesh
- ✓ Determine the relative stability of these surfaces at high temperatures
  - ✓ Constant-temperature ab initio molecular dynamic simulations.
  - ✓ Asymmetrical slab of (3x3) surface unit cell (8-9 Monolayers).
  - ✓ Brillouin zone sampling: Γ point

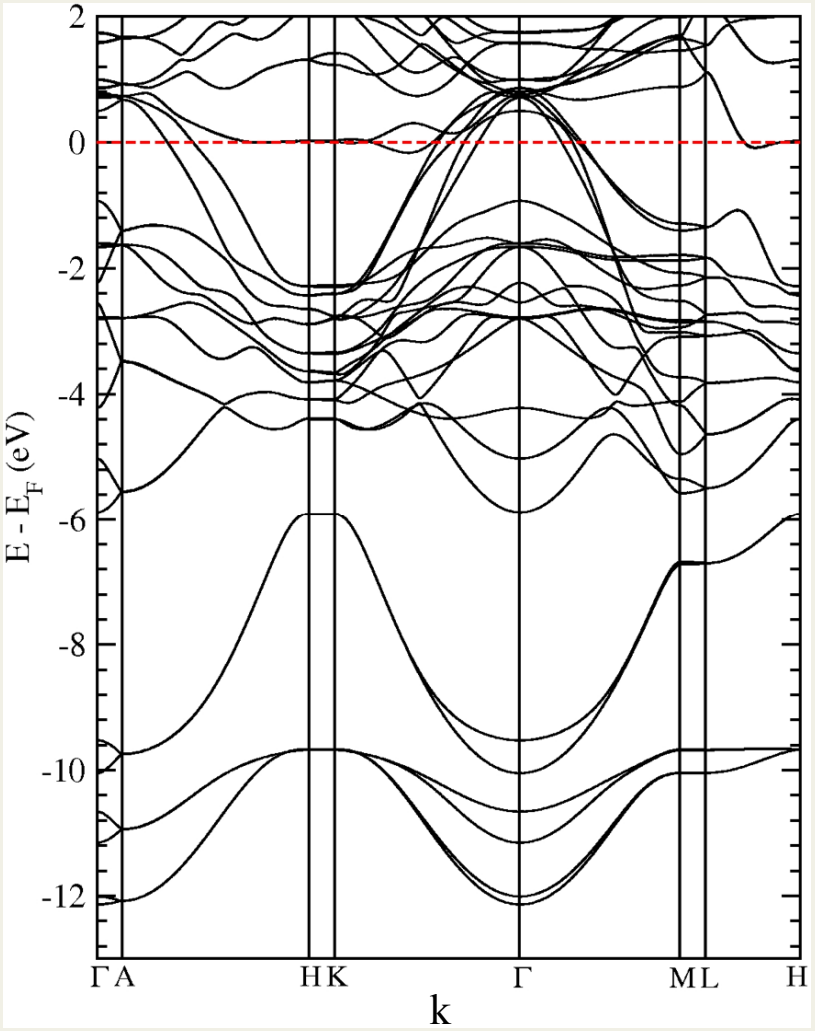
* W. Orellana & G. Gutiérrez, Surface Science **605**, 2087 (2011)

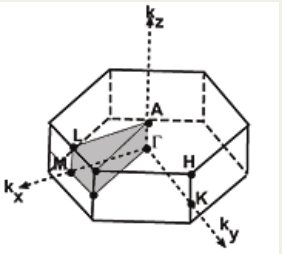
Electronic properties of bulk Ti_3SiC_2

Ti_3SiC_2 unit cell



Ti_3SiC_2 band structure

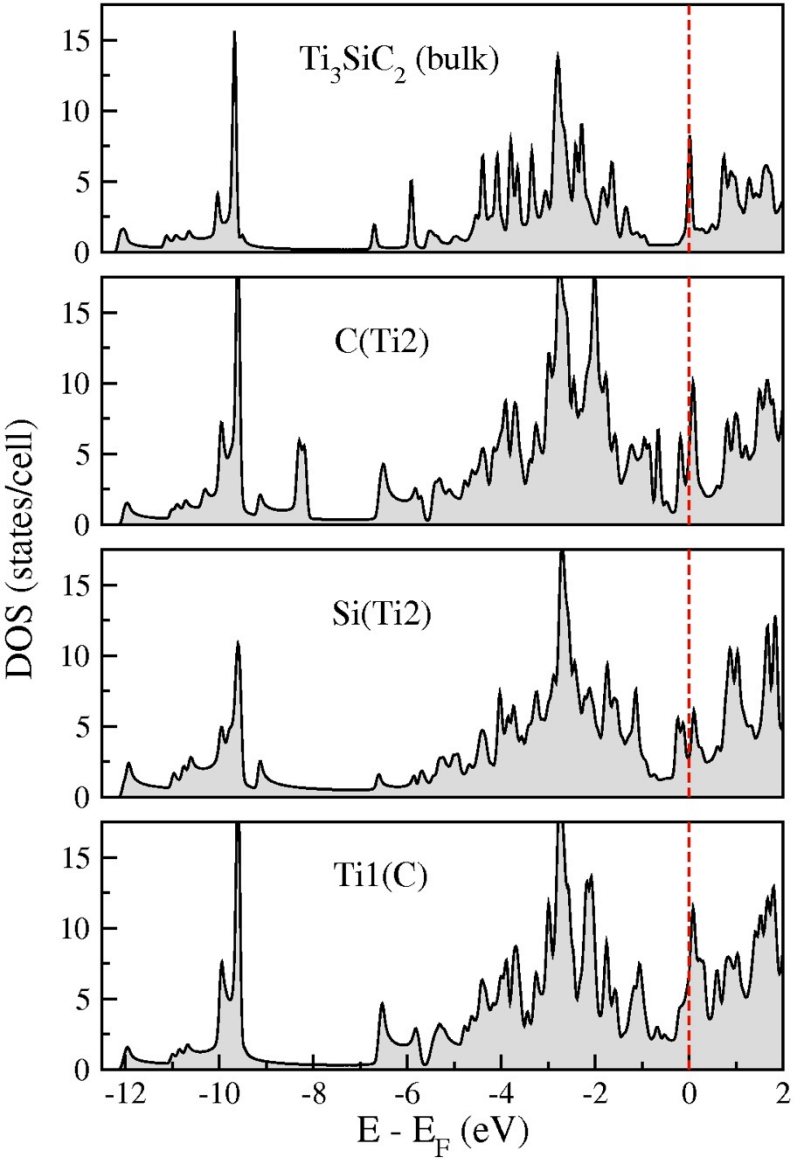




a = b = 3.08 Å (+0.5%)
c = 17.71 Å (+0.2%)

} Equilibrium lattice constants (deviation from experiments)

Electronic Properties



Surface Calculations

Bulk Ti_3SiC_2 has two kind of bonds for titanium: C-Ti1-C and C-Ti2-Si, giving six terminations along the (0001) direction: C(Ti1), C(Ti2), Si(Ti2), Ti1(C), Ti2(C), Ti2(Si).

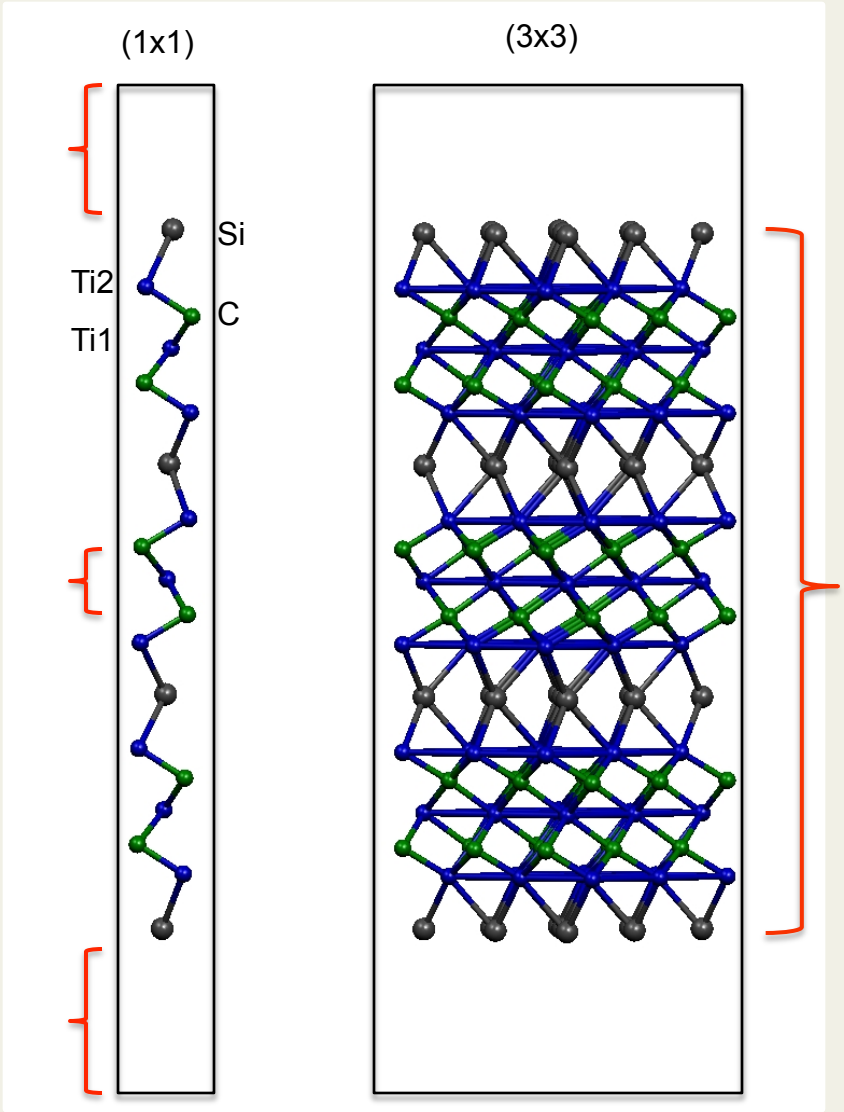
Si(Ti2) surface:

(1x1) topview

vacuum

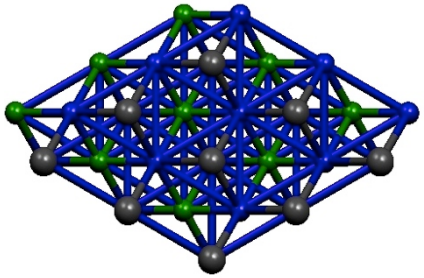
3 monolayer are fixed in the bulk geometry

vacuum



19 atomic monolayers

(3x3) topview



Surface Energy

Surface energy of a symmetrical-terminated slab at zero temperature and negligible pressure is given by

$$\gamma = (E_t - \sum n_i \mu_i)/2A$$

E_t = total energy of the slab
A = area of the slab
n_i = number of the atomic species i=C,Si,Ti
μ_i = chemical potential of the species i

- the chemical potentials μ_i are constrained to vary according to the MAX phase stoichiometric relation

- μ_i takes the value of its respective bulk phase

Relative surface stability

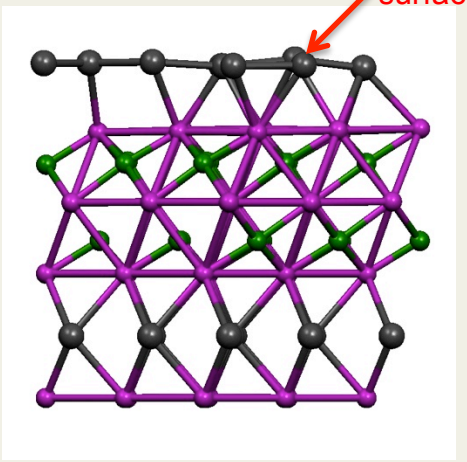
Surface	Mono layer	E_R (eV) (3x3)	γ (J/m^2) (3x3)	E_R (eV) (1x1)	γ (J/m^2) (1x1)
C(Ti1)	21	-17.15	8.49	-0.47	11.82
C(Ti2)	23	-3.74	8.45	-0.84	8.59
Si(Ti2)	19	-3.27	1.82	-0.07	2.57
Ti1(C)	19	-0.10	2.53	-0.29	2.65
Ti2(C)	23	-0.02	3.98	-0.10	4.15
Ti2(Si)	21	-0.43	1.88	-0.08	1.96

Si(Ti2) and Ti2(Si) show the lower-surface-energy terminations suggesting higher relative stabilities. We also observe large relaxation energies (E_R) in Si(Ti2) and carbon-terminated surfaces indicating reconstructions.

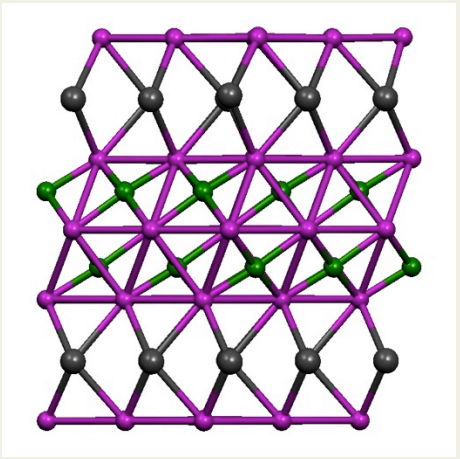
Previous calculations considering (1x1) surface unit cells show different results which we attributed to the minimal cell size used, which prevent on-plane relaxation.
Zhang *et al*. Acta Materialia 55, 4645 (2007).

Equilibrium Geometries

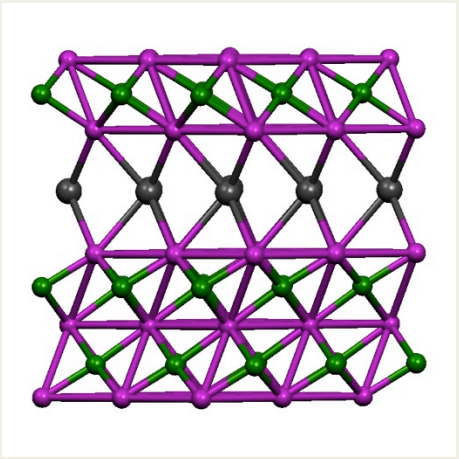
Si(Ti2) reconstructed surface



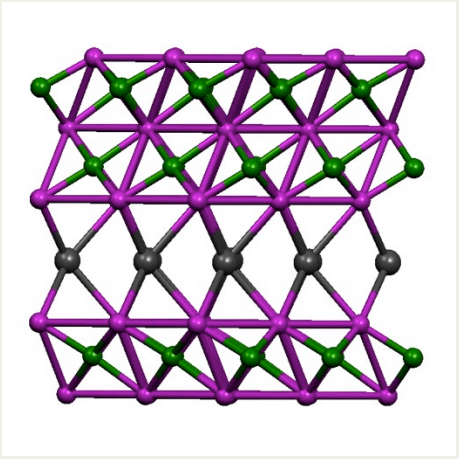
Ti2(Si)+0.1 eV



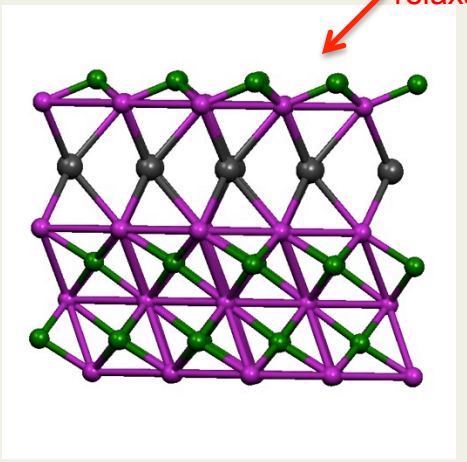
Ti1(C)+0.7 eV



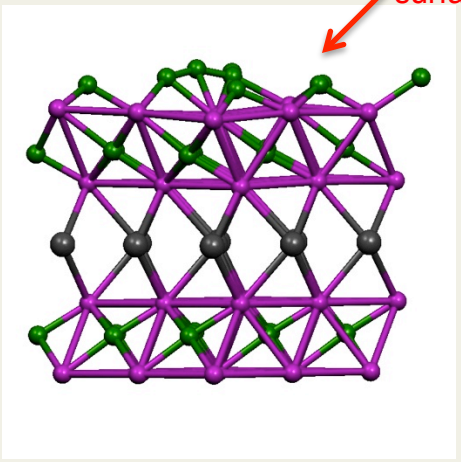
Ti2(C)+2.2 eV



C(Ti2)+6.6 eV large relaxation



C(Ti1)+6.7 eV reconstructed surface



Comparing average bond distances of Si-Ti [from Si(Ti2)] and Ti-C [from C(Ti2)], 2.73 and 1.94 Å, respectively, we confirm the weakness of the Si-Ti bonds.

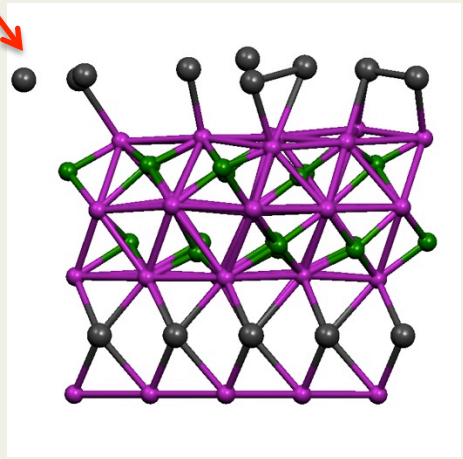
Stability at High Temperature: MD simulations

- ✓ Constant-temperature ab initio molecular dynamic simulations
- ✓ Asymmetrical slab with 8-9 monolayers, fixing the two bottommost.
- ✓ T = 800, 1000, 1200, and 1400 °C, over 4 ps with a time step 1 fs.

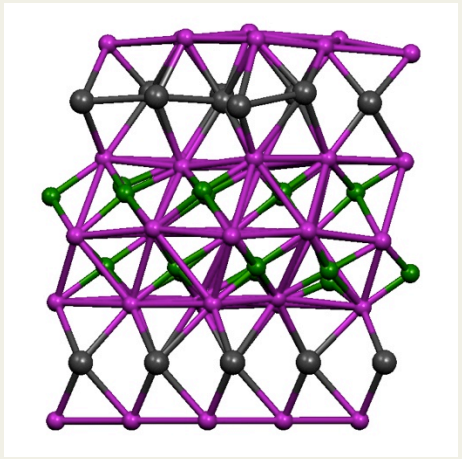
Snapshot of MD simulations at 1400 °C

desorptions

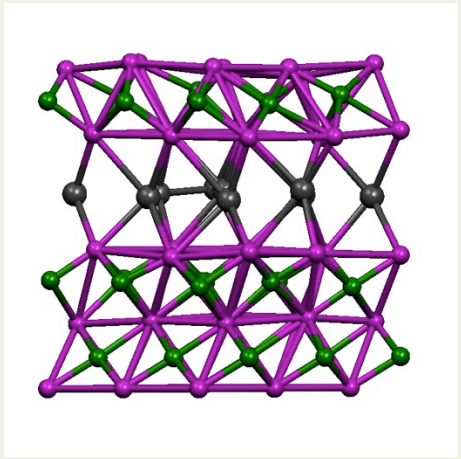
Si(Ti2)



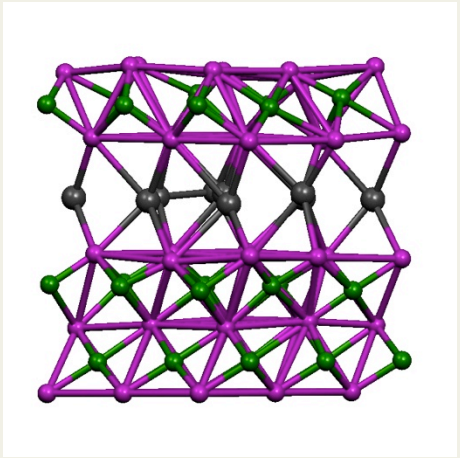
Ti2(Si)



Ti1(C)

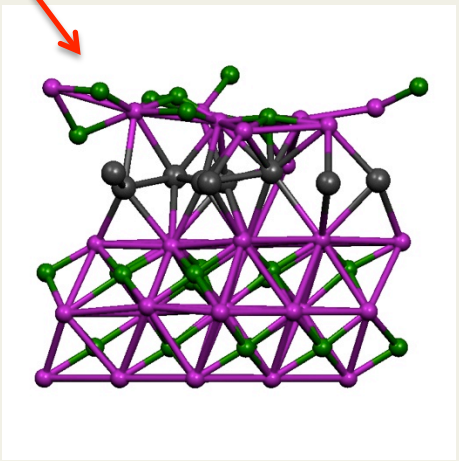


Ti2(C)



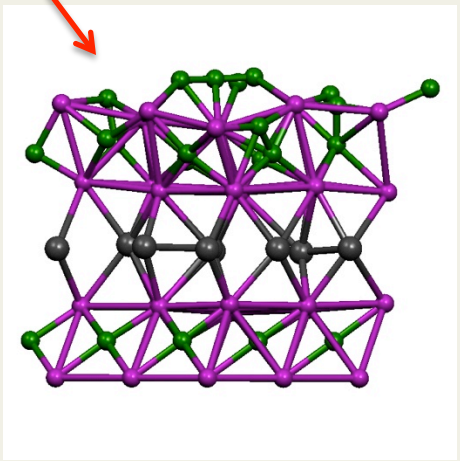
amorphization

C(Ti2)



amorphization

C(Ti1)

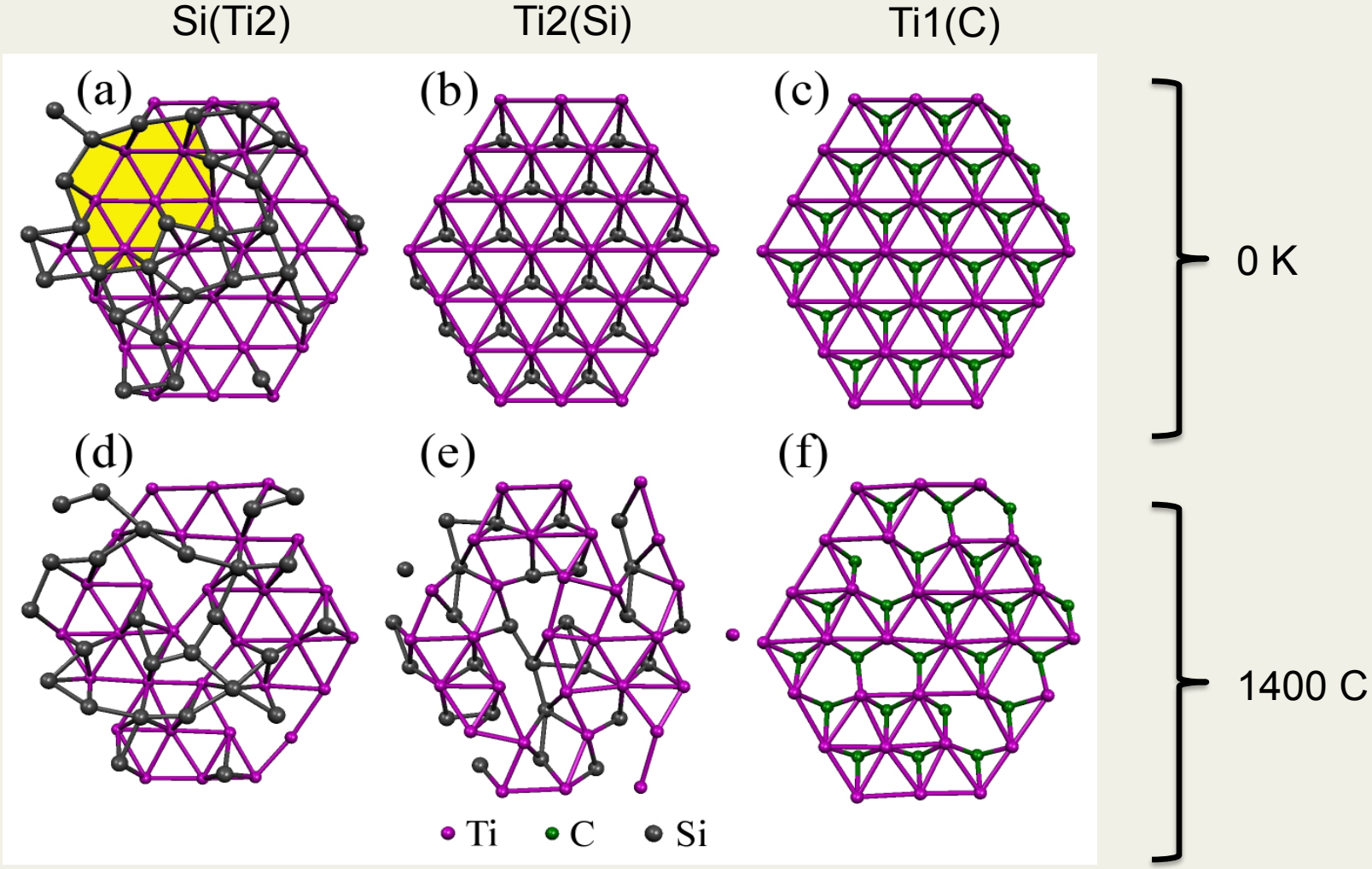


The weakness of the Si-Ti bonds as compared with C-Ti provoke large Si displacements inducing surface amorphizationand and desorptions when the Si ML is close to the topsurface

MD simulations at 1400 °C

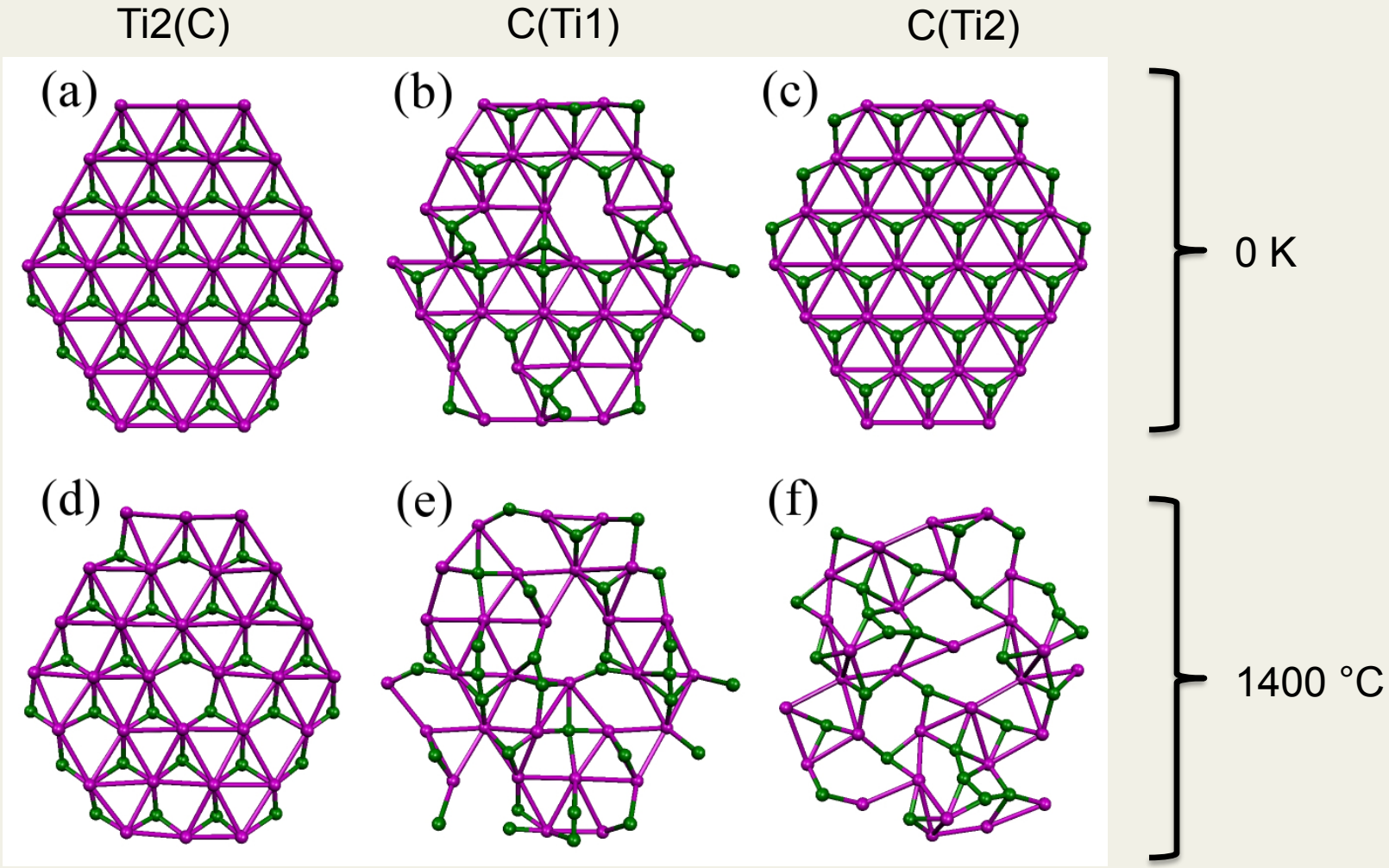
See animation

Stability at 0K and high temperature



- ✓ Si(Ti2) shows low surface energy at 0K, however it is highly unstable at high temperatures, forming a liquid phase at topsurface and desorption event.
- ✓ Si(Ti2) when located at subsurface induces topsurface amorphization.

Stability at 0K and high temperature

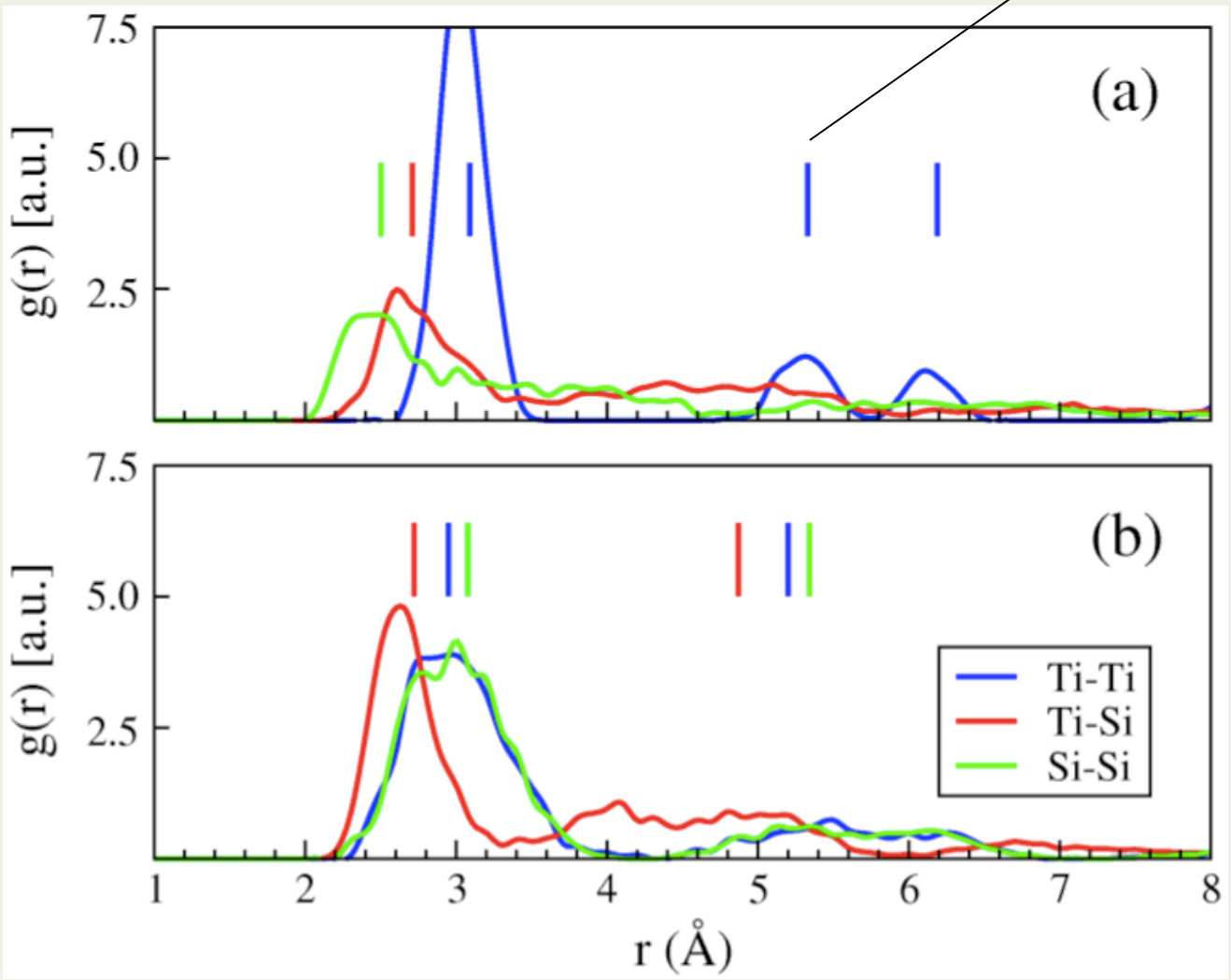


- ✓ Ti1(C) and Ti2(C) although with higher surface energy, show a remarkable thermal stability at high temperatures, preserving their structures up to 1400 °C.
- ✓ C(Ti1) and C(Ti2) show amorphization features with the formation of C-C covalent bonds.

Atomic structure at high temperature:1400 ºC

Pair distribution function

at 0 K after reconstruction



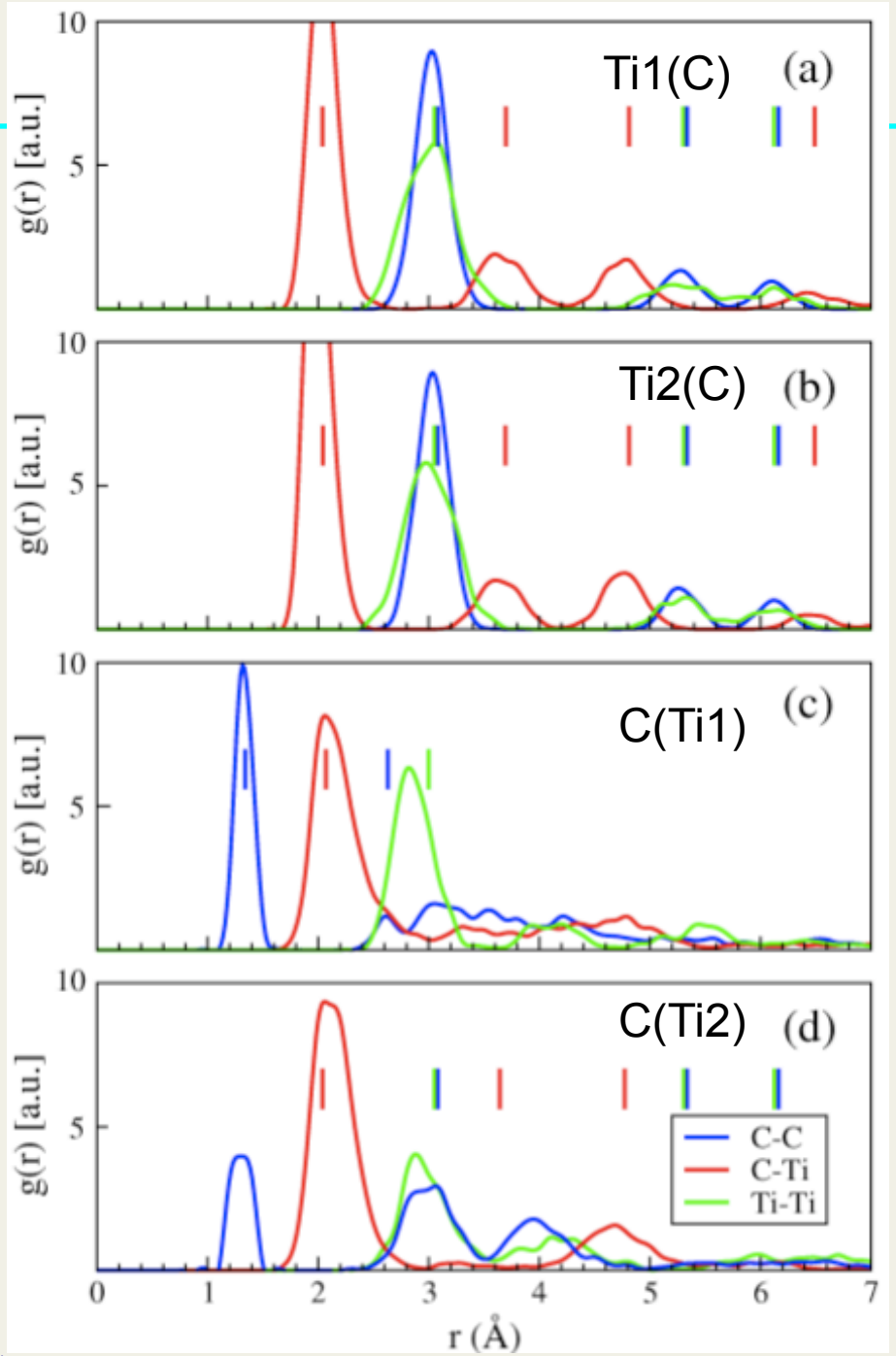
Si(Ti2)

Si-Si and Ti-Si have liquid-like structure

Ti2(Si)

Si subsurface layer induce disorder in Ti top layer

Atomic structure at high temperature:1400 ºC

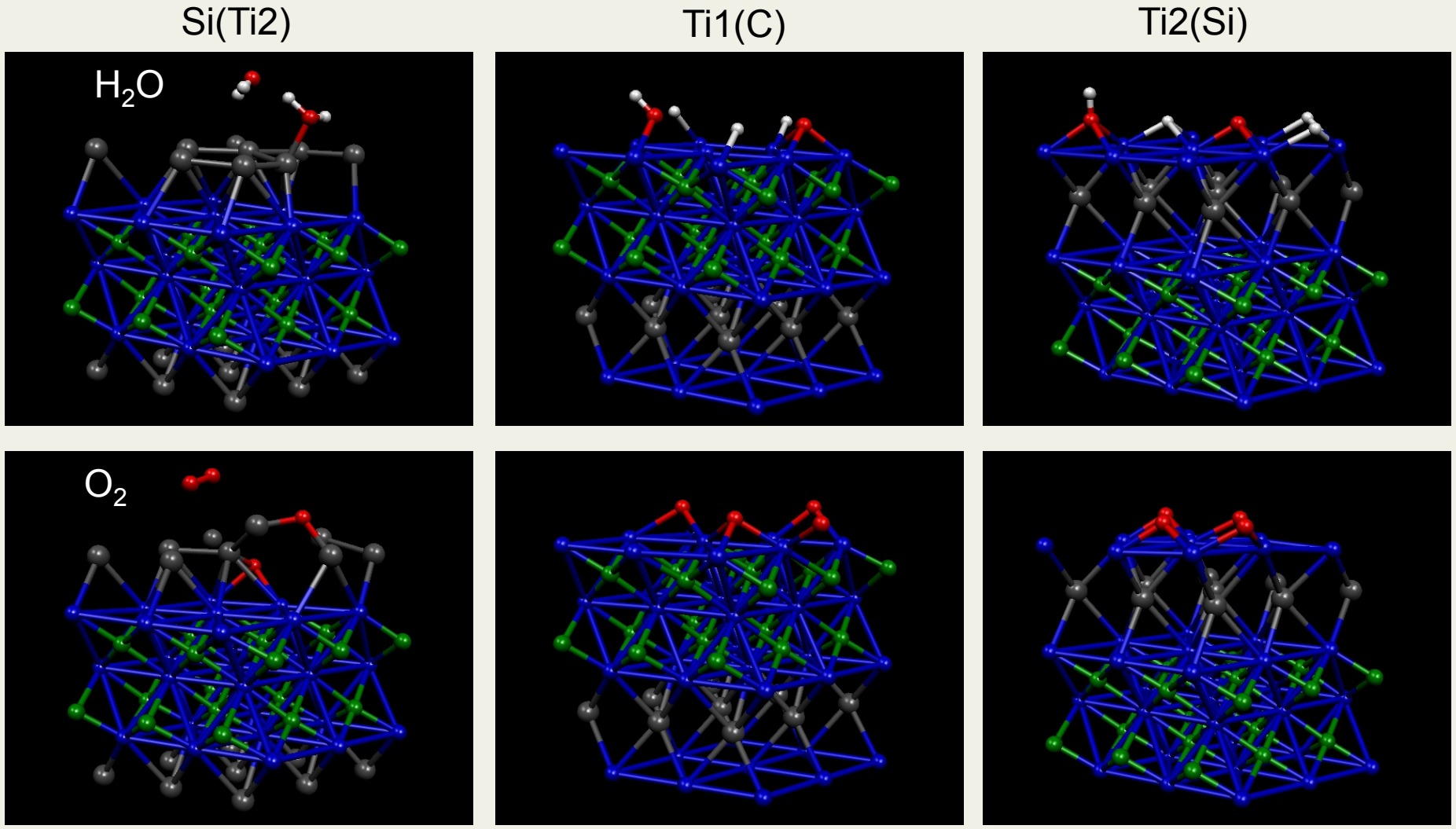


Well defined peak for C-Ti and C-C, less defined Ti-Ti.
Basically crystalline order

Short range order in C-C and C-Ti

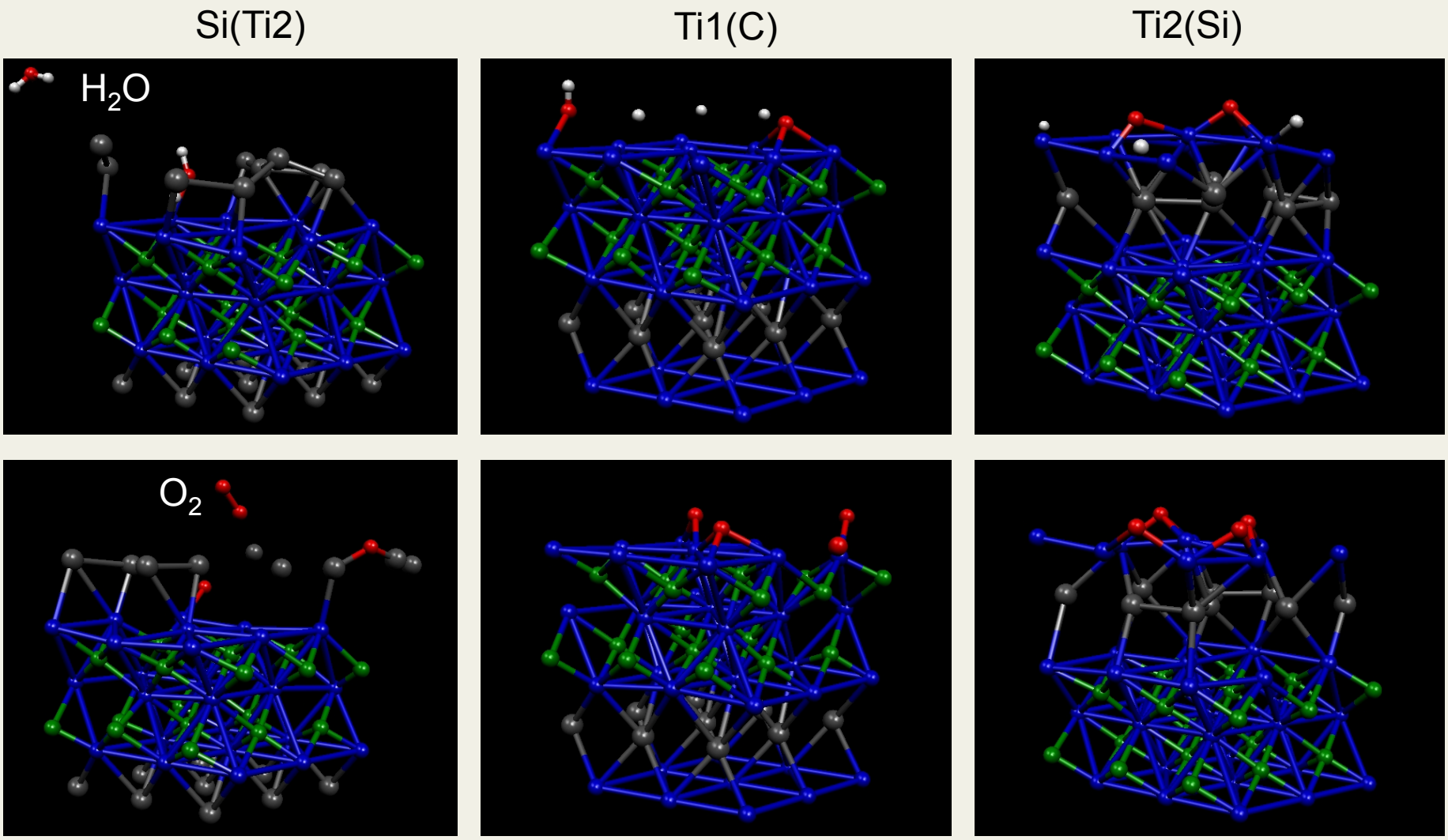
C-C bond formation induced by temperature

Surface oxidation by H_2O and O_2 at 0K



- ✓ Two molecules of the same species are released at 3 Å from the surfaces without constraints.
- ✓ On Si(Ti2), H_2O do not react with the surface while O_2 forms SiO species after dissociation. On Ti1(C) and Ti2(Si) both molecules instantaneously dissociate after reaching the surfaces forming a TiO toplayer.

Surface oxidation by H_2O and O_2 at 1400 °C



- ✓ Snapshots of MD simulations at 1400 °C for H_2O and O_2 molecules reacting with the surfaces.
- ✓ Si-O species are removed from the Si(Ti2) surface after O_2 dissociative reactions. Meanwhile,
- ✓ on Ti2(Si) and Ti1(C), a highly stable TiO toplayer are formed. Oxygen diffusion inside the material is not observed.

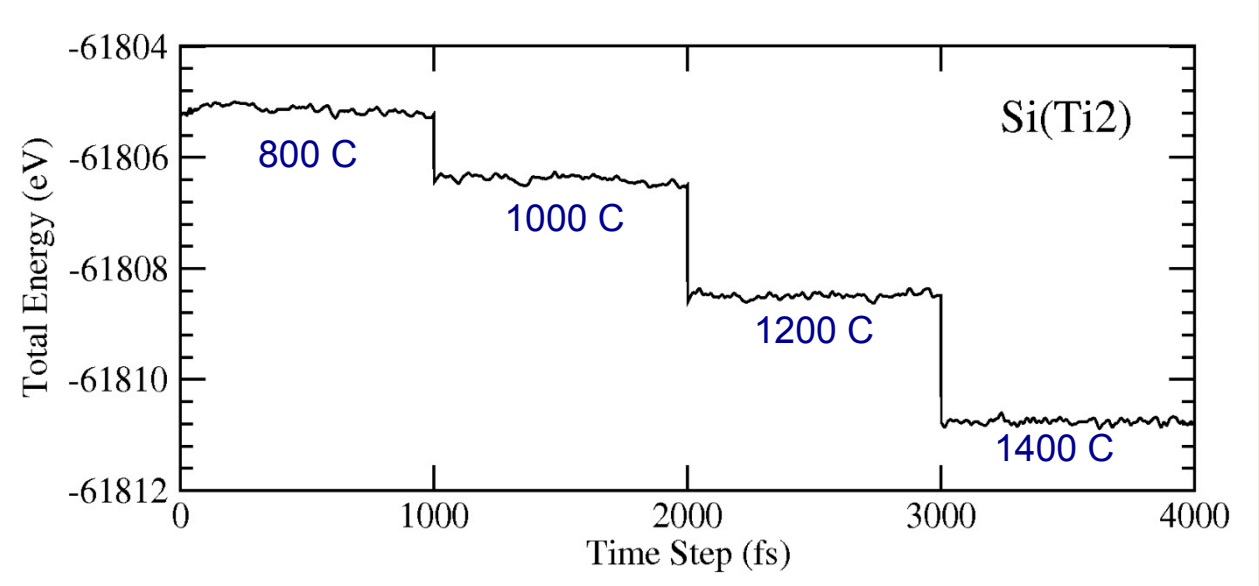
Conclusions

- ✓ Si(Ti2) and Ti2(Si) have the lower surface energy at 0K suggesting stable surfaces.
- ✓ Ti1(C) and Ti2(C) although with higher surface energy, show a remarkable thermal stability, preserving their structure up to 1400 °C.
- ✓ The common association of high surface stability with low surface energy at 0K cannot be extrapolated at higher temperatures.

Thank you!

Stability at High Temperature: MD simulations

- ✓ Constant-temperature ab initio molecular dynamic simulations (NVT ensamble).
- ✓ Asymmetrical slab with 8-9 monolayers, fixing the two bottommost.
- ✓ T = 800, 1000, 1200, and 1400 °C, over 4 ps with a time step 1 fs.



Total energy variation with temperature for the Si(Ti2) surface under constant thermalization at the chosen temperatures during 1 ps.