Adhesive strength of interfaces between bcc and fcc Fe and transition metal carbides: effect of misfit dislocations on structure and bonding

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Motivation

- **Dispersed inclusions of carbides *MC* (*M* is Ti, V, Nb, Mo) provide superior fracture toughness and increased strength for ferritic steels**
- ***MC* precipitates in austenitic stainless steels are formed with Ti, V, Nb, Zr additions, resulting in improved:**
  - **Strength**
  - **Creep resistance**
  - **Intergranular corrosion resistance**

Objectives

- **Investigate interfacial adhesion of the ferrite and austenite phases of Fe and transition metal carbides *M*C, where *M* is (Ti, V, Nb, Mo)**
- **Understand the interface adhesion at the atomic and electronic levels**
- **Evaluate the effect of misfit dislocations on structure, bonding and adhesive strength of interfaces**

Methodology

- **First-principles calculations based on density functional theory (DFT)**
- **Use of highly precise full-potential linearized augmented plane wave (FLAPW) method [1]**

[1] E.Wimmer, H.Krakauer, M.Weinert, and A.J.Freeman, PRB 24, 864 (1981) : Film method
H.J.F. Jansen and A.J.Freeman, PRB 30, 561 (1984) : Bulk method

Difficulties in modeling austenitic steel/MC interfaces

- **Significant and varying content of alloying additions to Fe, most notably Cr (18%) and N (10%)**
- **Large lattice misfit between fcc Fe and *M*C (15-20%)**
- **Non-stoichiometry in *M*C**
- **Substitution of *M* with Cr**
- **More complex precipitate phases possible (Z-phase, $M_{23}C_6$, σ-phase)**

bcc Fe/*MC* lattice misfit

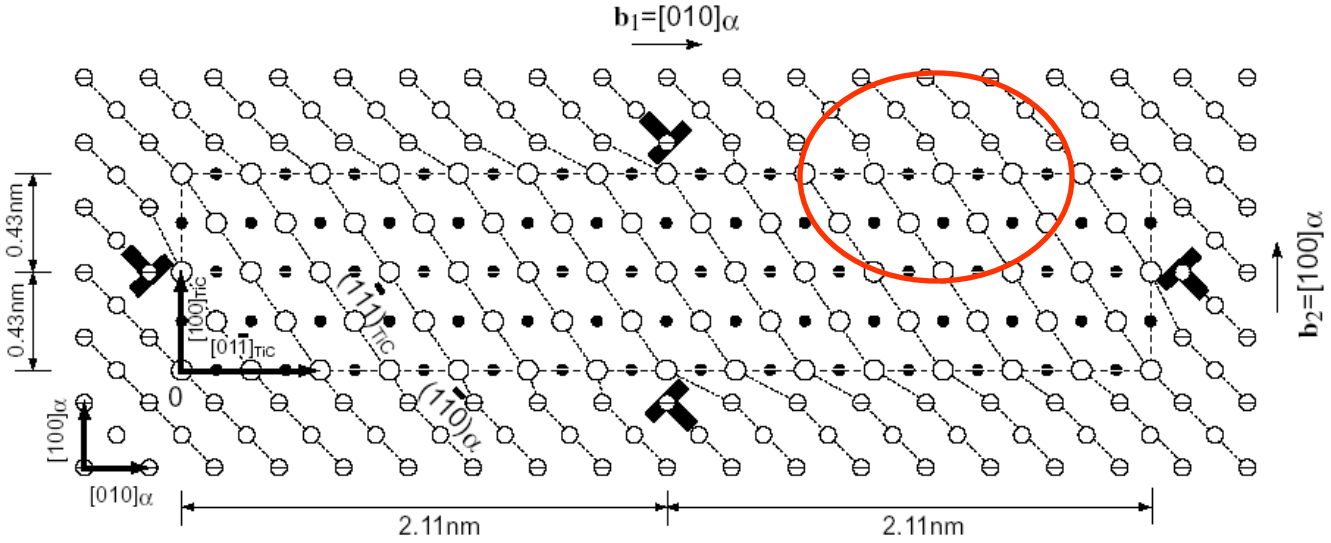
Lattice constants and misfit δ:

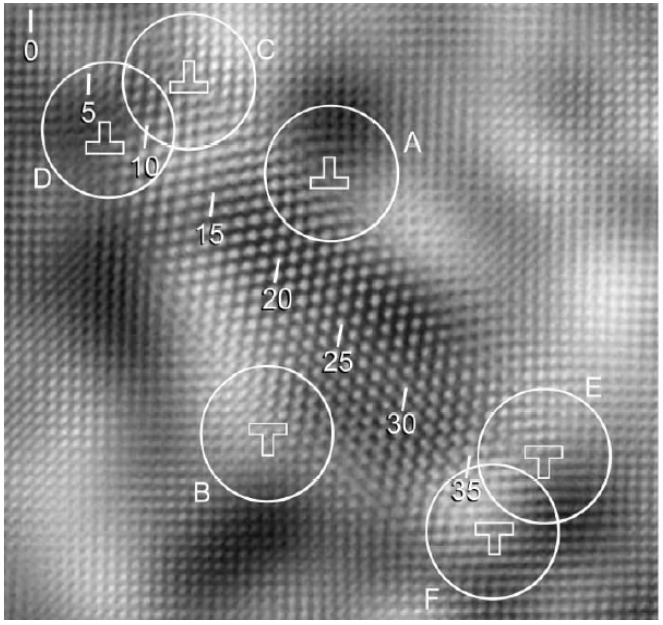
$$\delta = \frac{a_{MC} - \sqrt{a_{Fe}}}{\frac{1}{2}(a_{MC} + \sqrt{a_{Fe}})}$$

	bcc Fe	TiC	VC	NbC	MoC
Lattice constants (Å)	2.86	4.32	4.18	4.43	4.28
Misfit (%)	–	6.4	3.3	8.7	5.6

- Small lattice misfit suggests that coherent interfaces could be possible

Adhesion of coherent bcc Fe/*M*C interfaces (*M* = Ti, V, Nb, Mo)





- **Coherent patches on "top" facet of precipitate**

F.G Wei, T. Hara and K. Tsuzaki, Philos. Mag. 84, 1735 (2004)

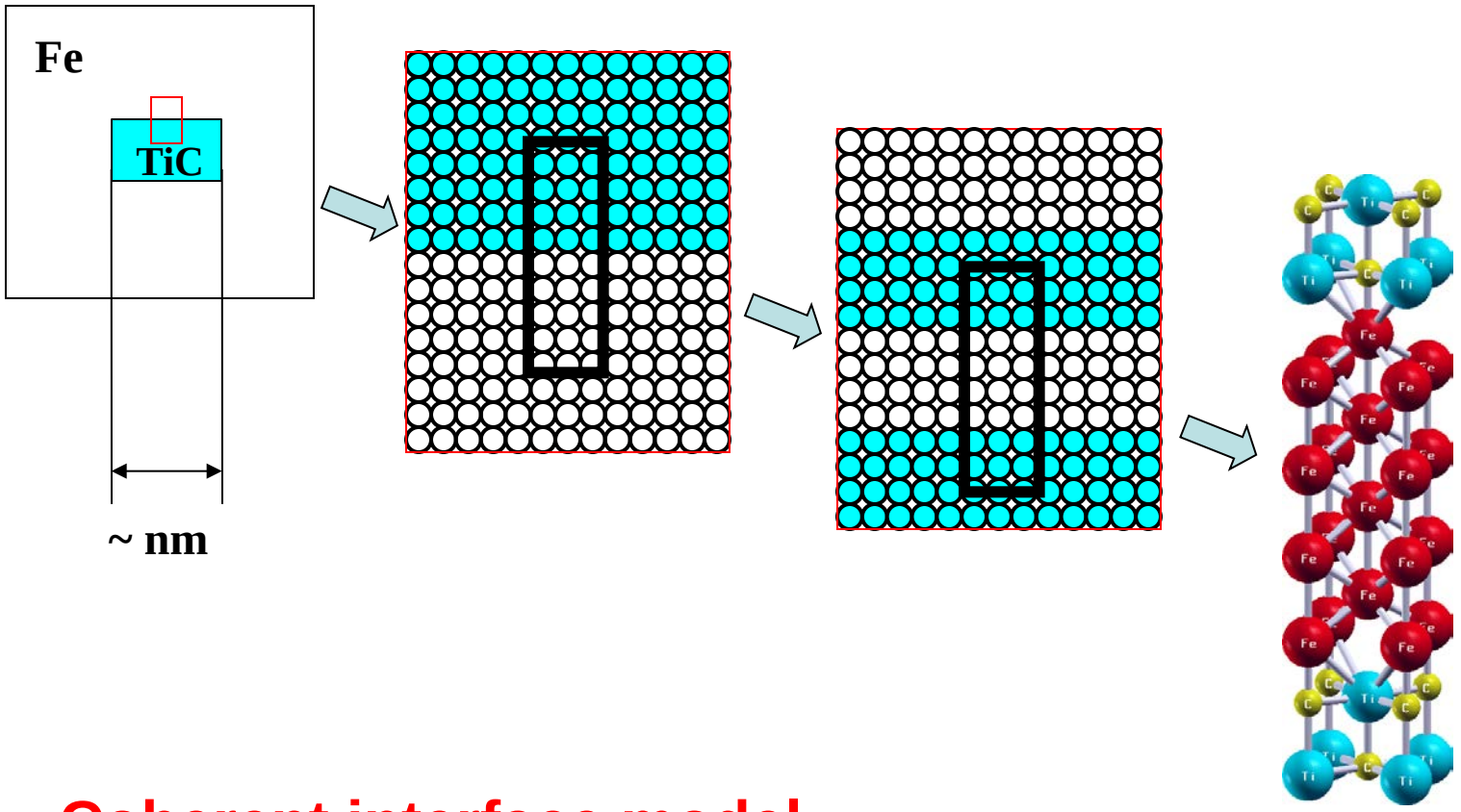
fcc Fe/*M*C interface: lattice misfit

$$\delta = \frac{a_{MC} - a_{Fe}}{\frac{1}{2}(a_{MC} + a_{Fe})}$$

	fcc Fe	TiC	VC	NbC	MoC
Lattice constants (Å)	3.42	4.32	4.18	4.43	4.28
Misfit (%)	–	21.3	18.0	23.7	20.3

- Large lattice misfit – no coherent interfaces possible

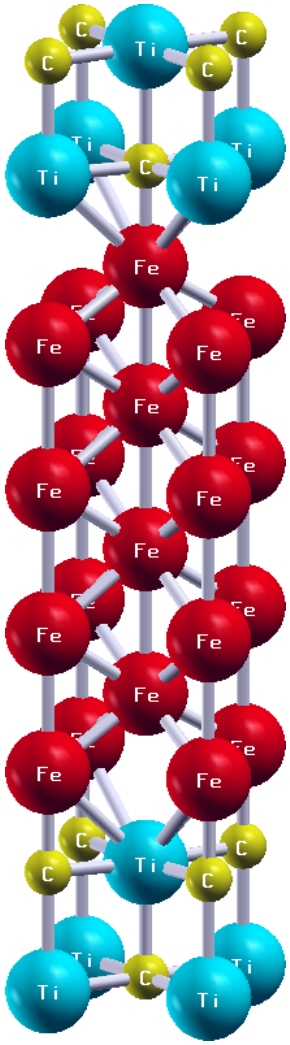
Interface structure model



- Coherent interface model
- Calculations using superlattice approach

Interface structure models

bcc Fe/TiC

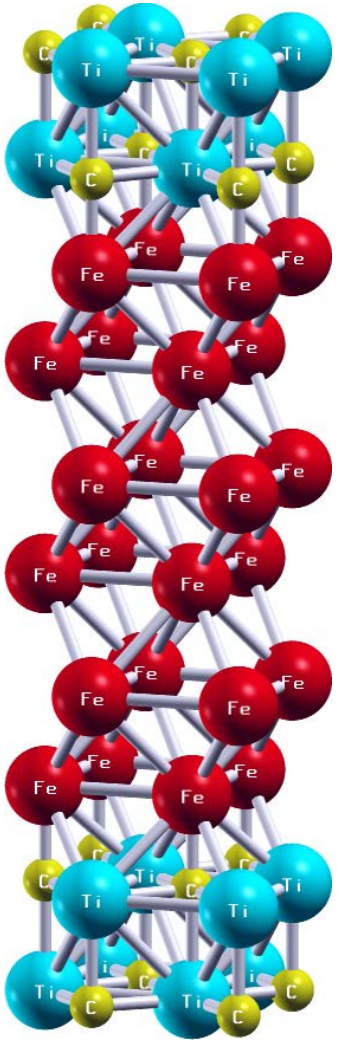


- **Superlattice model**
- **Baker-Nutting orientation:**

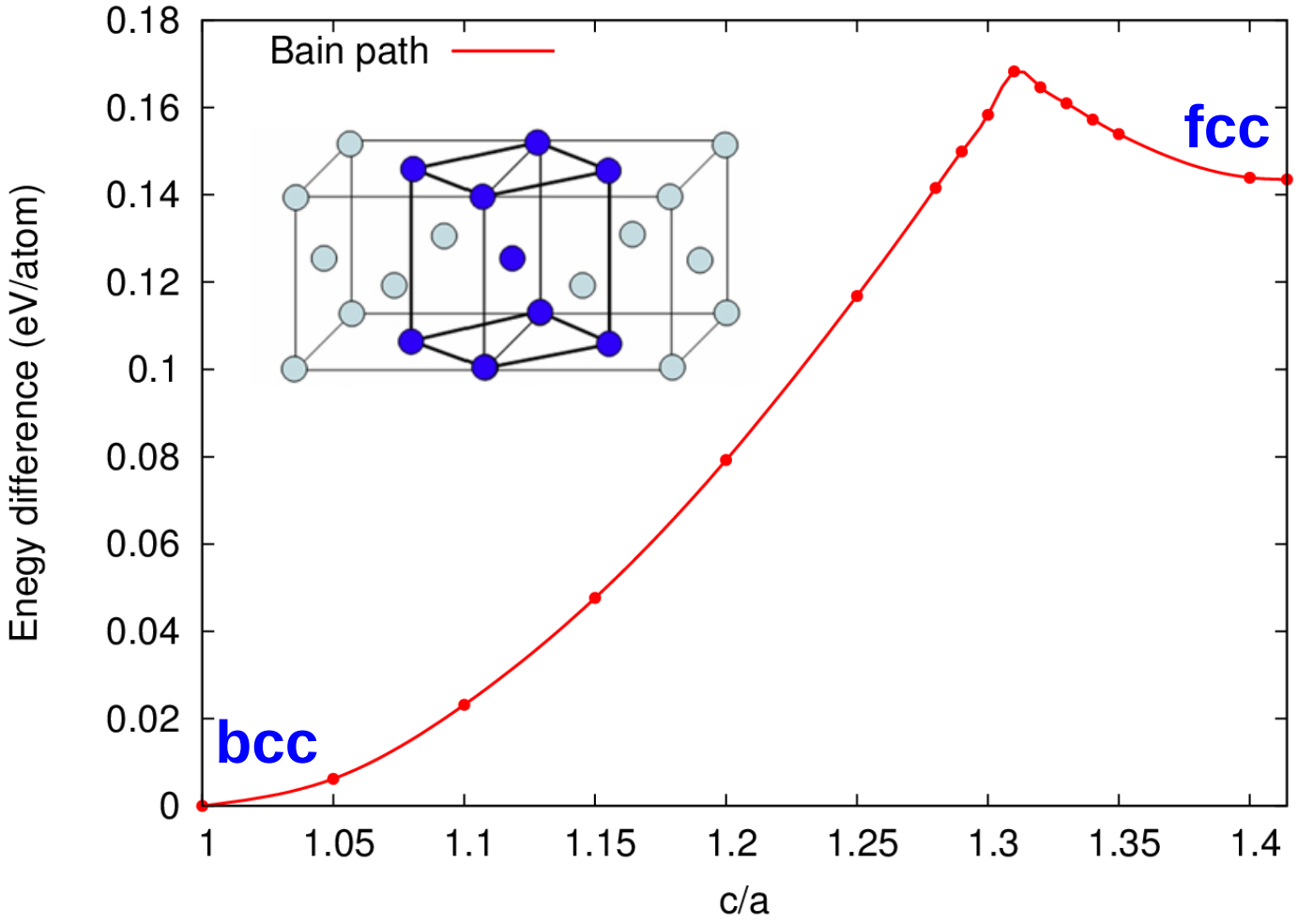
$$(001)_{MC} \,//\, (001)_{bcc}$$
$$[100]_{MC} \,//\, [110]_{bcc}$$
$$(001)_{MC} \,//\, (001)_{fcc}$$
$$[100]_{MC} \,//\, [100]_{fcc}$$

- **Optimized atomic positions**
- **Optimized *c* length**
- **Site-preference is fully considered**

fcc Fe/TiC

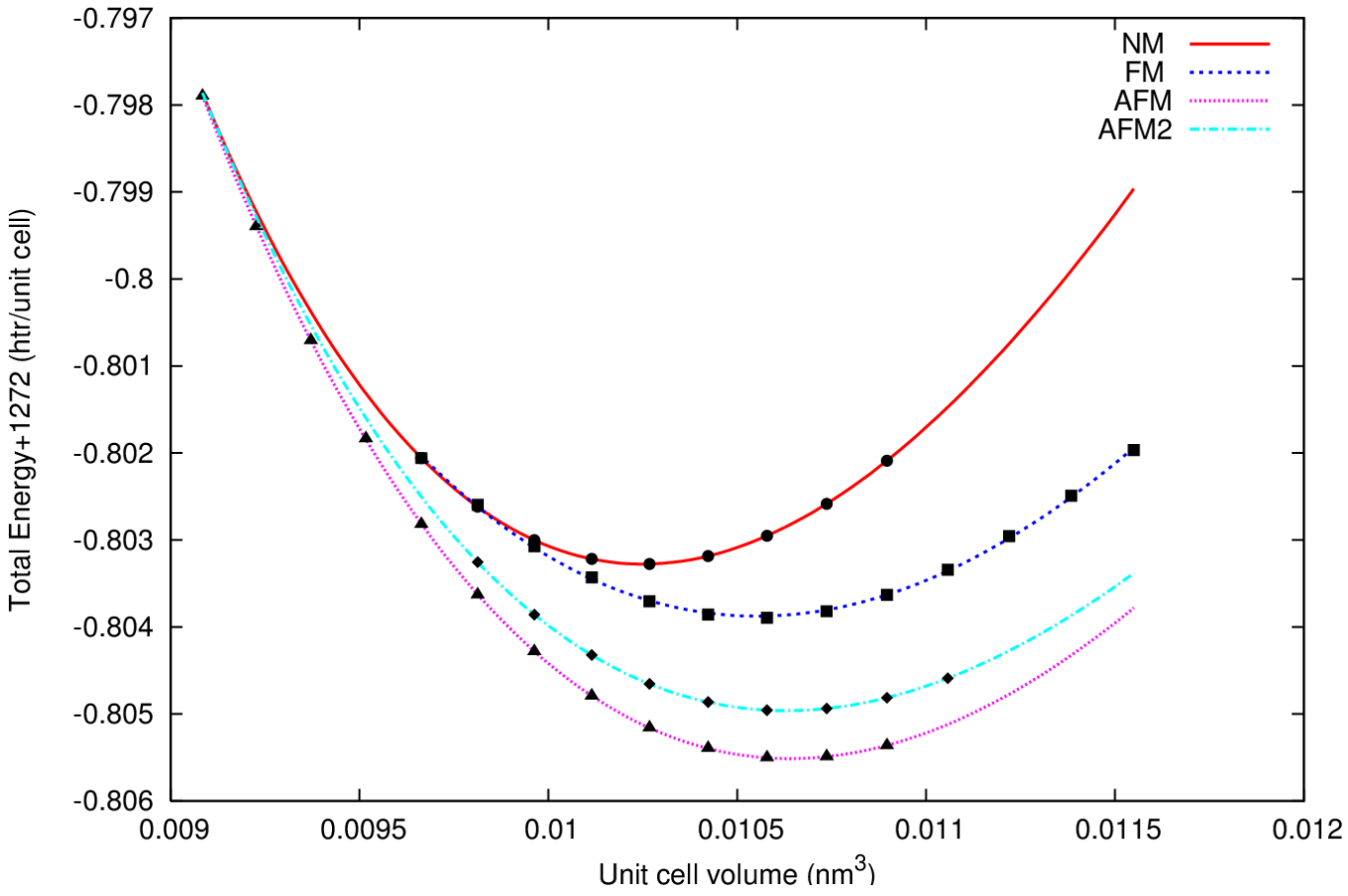


bcc-fcc relation: Bain path



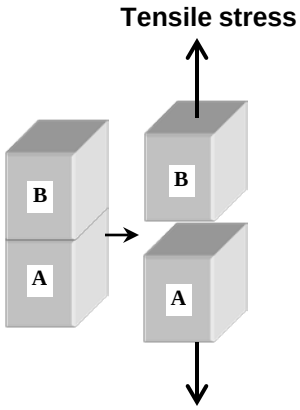
- **fcc structure may collapse into bcc structure upon tetragonal compression**

Magnetism of fcc Fe



- **Complex magnetism of fcc Fe with multiple competing magnetic structures**

Fe/*MC* work of separation

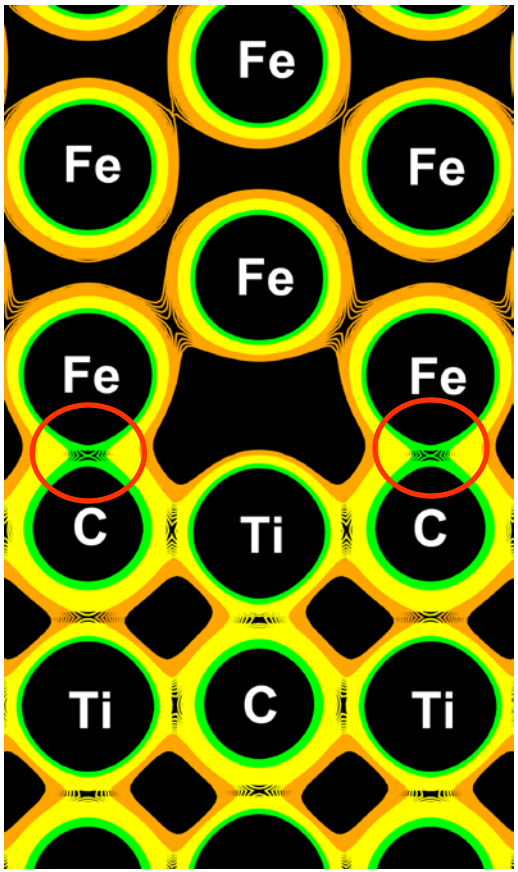


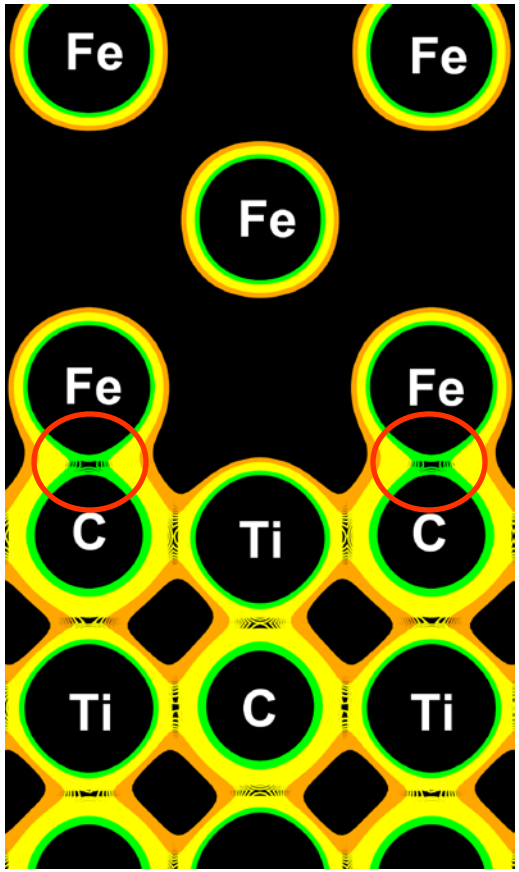
Calculated work of separation (J/m^2)

	Fe/TiC	Fe/VC	Fe/NbC	Fe/MoC
bcc Fe	3.60	3.78	3.69	3.58
fcc Fe	3.63	3.81	3.78	3.80

- Very high work of separation for all cubic carbide-bcc Fe interfaces suggests strong interfacial adhesion
- Work of separation is largest for Fe/VC interface
- Very high work of separation for all cubic carbide-fcc Fe interfaces
- Work of separation is similar to carbide-bcc Fe interfaces – similar interfacial bonding?

Electronic origins of strong interface adhesion: charge density



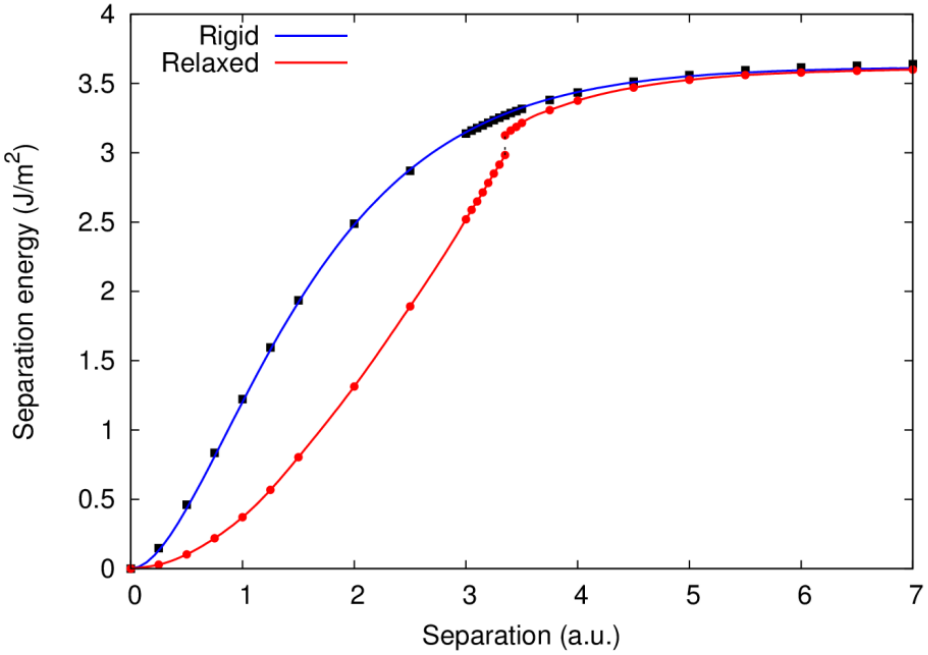


- **Strong covalent bonding**
- **Short bonding distance**
- **Fe-C in bcc Fe/TiC: 1.89 Å**
- **Fe-C in fcc Fe/TiC: 1.90 Å**
  - **compare Fe_3C: 1.94 Å**

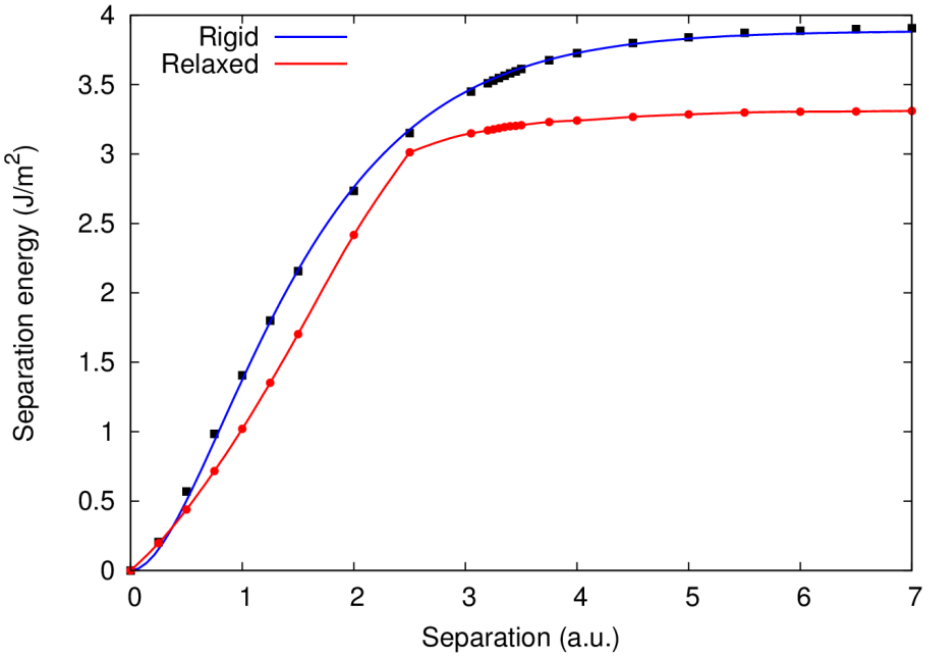
- **Short Fe-C bond length and charge accumulation indicates strong interfacs bonding of covalent character**
- **Almost indentical character of interfacial bonding**

Role of magnetism

AFM

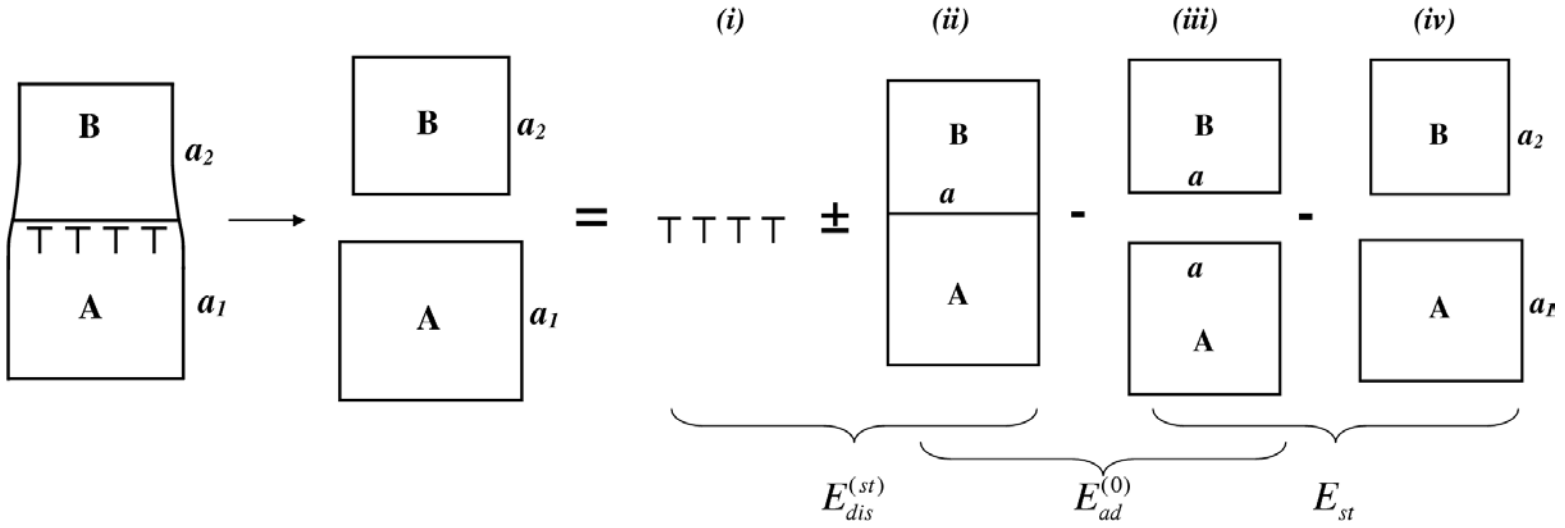


NM



- **Account for magnetism is necessary for accurate description of interface adhesion**

Cleavage of semicoherent interface

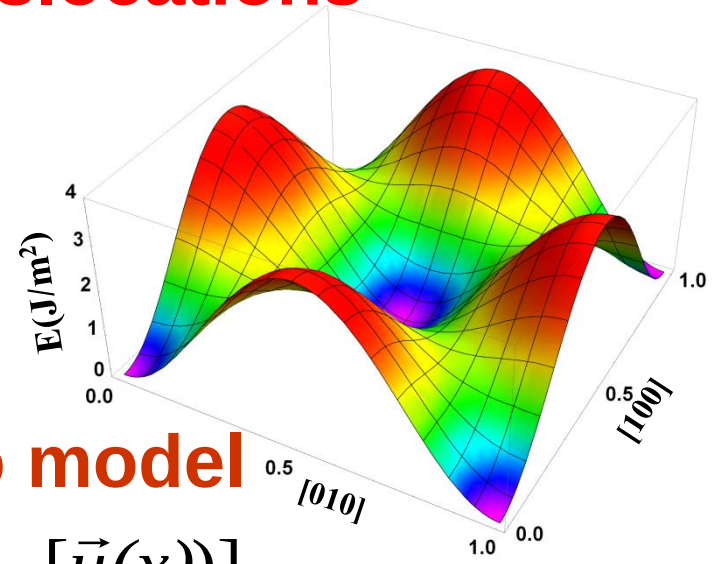


Adhesion energy: $E_{ad} = E_{ad}^{(0)} - E_{dis}$; $E_{ad}^{(0)}$ **- ideal work of separation**

Misfit dislocation energy: $E_{dis} = E_{dis}^{(st)} + E_{st}$; E_{st} **- strain energy**

Mistit dislocations at coherent interfaces

Combined *ab-initio*+Peierls-Nabarro model approach for misfit dislocations



1. *Ab-initio* GSF calculations

$\Phi(u)$ - generalized stacking fault (GSF) energetics

2. Modified 2D-Peierls Nabarro model

$$E_{tot}[\vec{u}(x))] = E_{misf}[\vec{u}(x))] + E_{elast}[\vec{u}(x))]$$

3. Solution of minimized PN functional

$$E_{tot}[\vec{u}(x))] = E_{tot}(\omega_\alpha, d_\alpha, l); \quad \{\omega_\alpha, d_\alpha, l\}$$ - dislocation geometry

$$p = \delta / a$$ - dislocation spacing

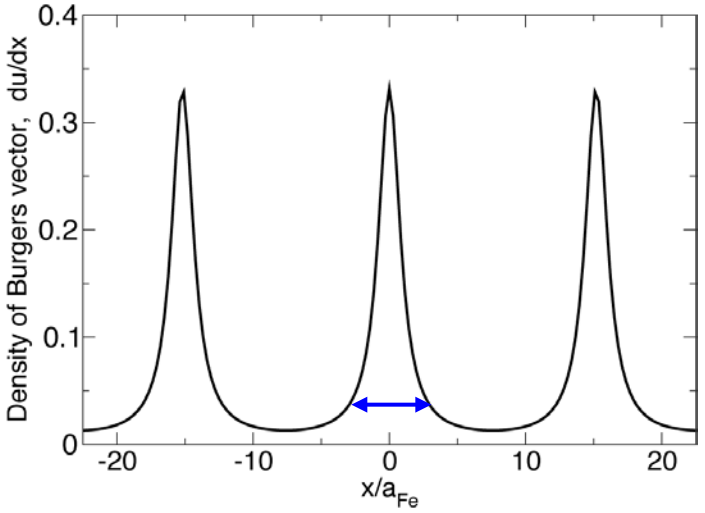
N.I. Medvedeva, Yu.N. Gornostyrev, O.Yu. Kontsevoi, and A.J. Freeman, Acta Mater. 58, 927 (2004)

bcc Fe/TiC: misfit dislocation energy and structure

Energetics [J/m^2]

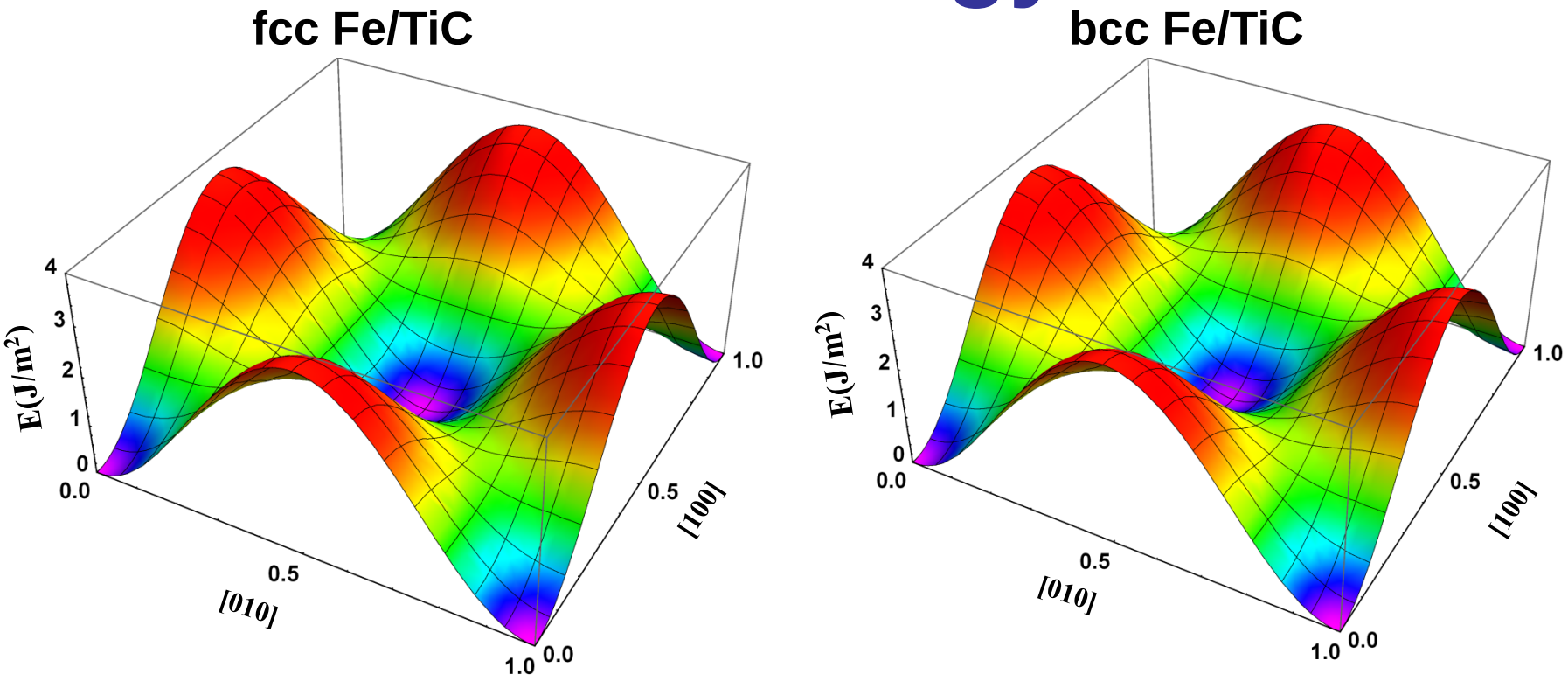
$E_{ad}^{(0)}$	E_{dis}	E_{ad}
3.60	0.70	2.90

Dislocation structure



- **Interface strength is decreased by 0.70 J/m^2 (~20%)**
- **Misfit dislocations are mobile, have a wide core (~ 4 a_{Fe}) and very low Peierls energy**
- **Crack activation on the interface will not occur**

fcc Fe/TiC interface: GSF energy



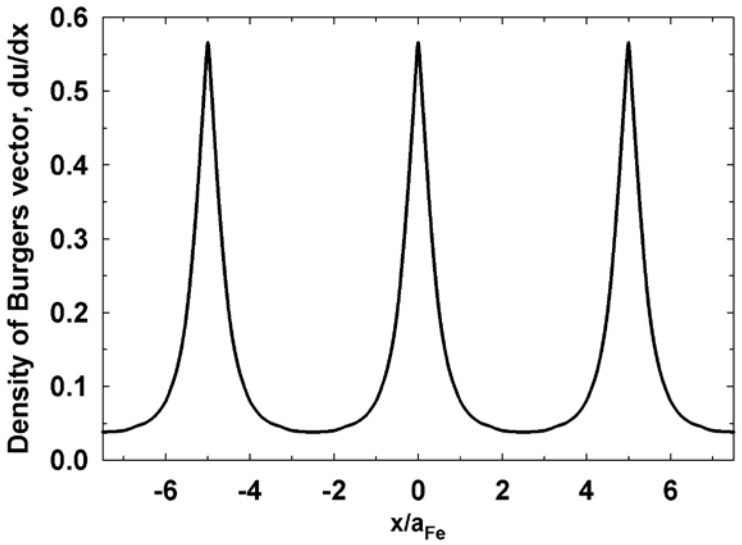
- Similar barriers to shear at fcc Fe/TiC and bcc Fe/TiC interfaces
- Misfit dislocation energy difference should originate from elastic contribution to Peierls energy

fcc Fe/TiC: misfit dislocation energy and structure

Energetics [J/m^2]

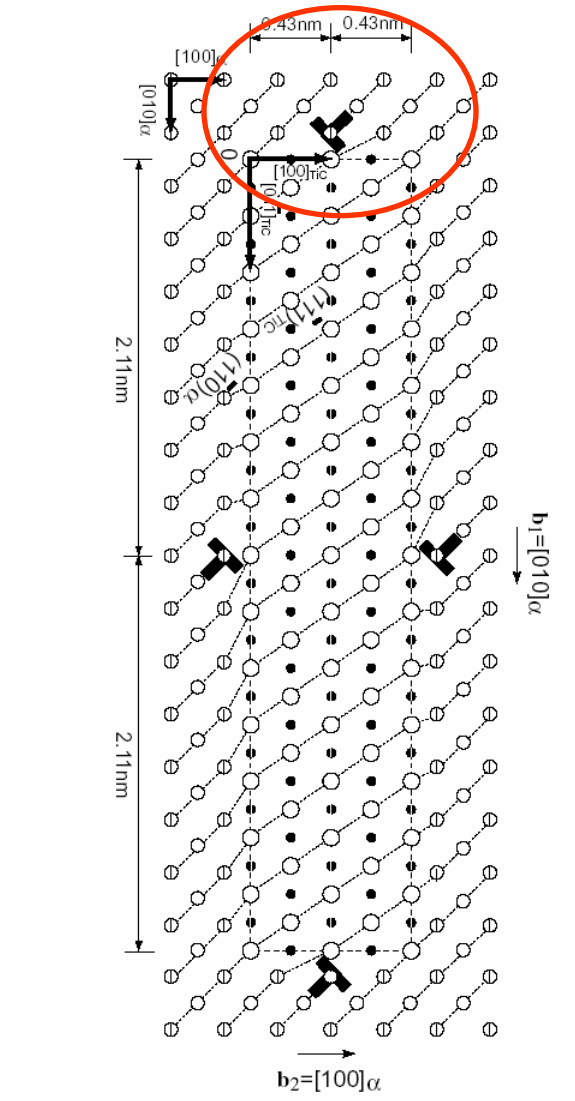
$E_{ad}^{(0)}$	E_{dis}	E_{ad}
3.63	1.40	2.23

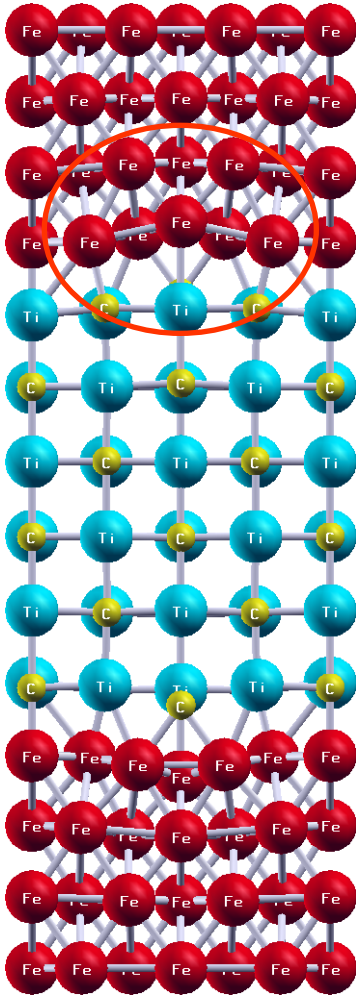
Dislocation structure



- Dense array of narrow-core (~ 1.5 a_{Fe}) misfit dislocations forming at the interface
- Relatively low mobility and high Peierls energy
- fcc Fe/TiC Interface strength is decreased by 1.4 J/m^2 (~40%)

bcc Fe/TiC semicoherent interface model

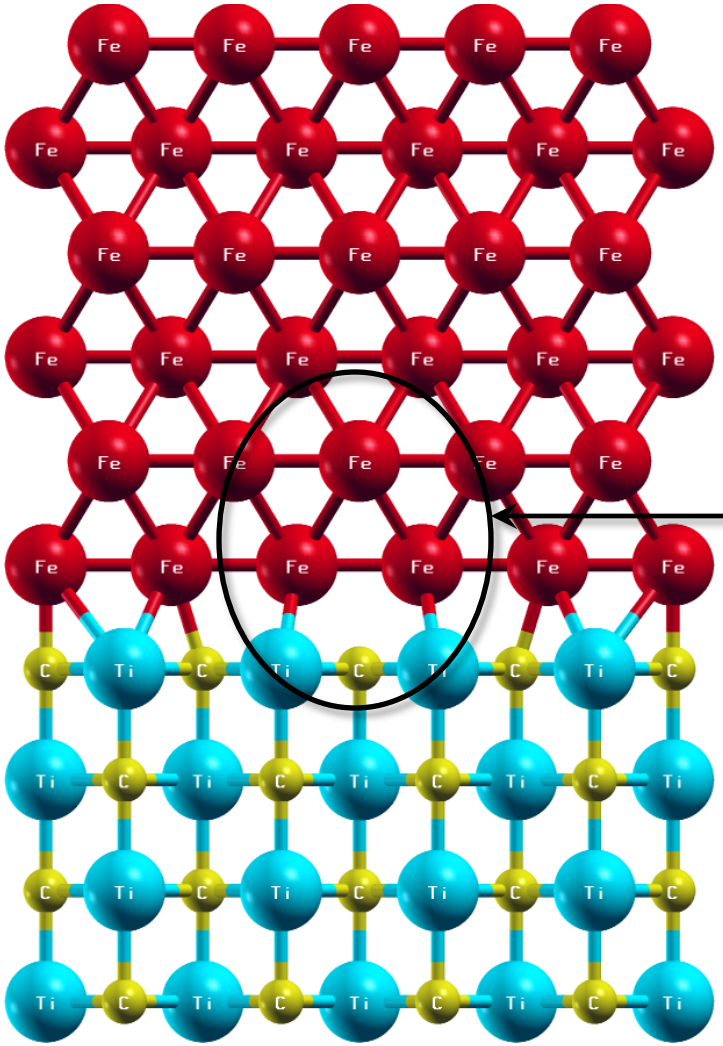




- $2a_{TiC}/3a_{Fe}$ matching in [100]
- $1a_{TiC}/1a_{Fe}$ matching in [001]
- 96 atoms

- Model contains one misfit dislocation per unit cell

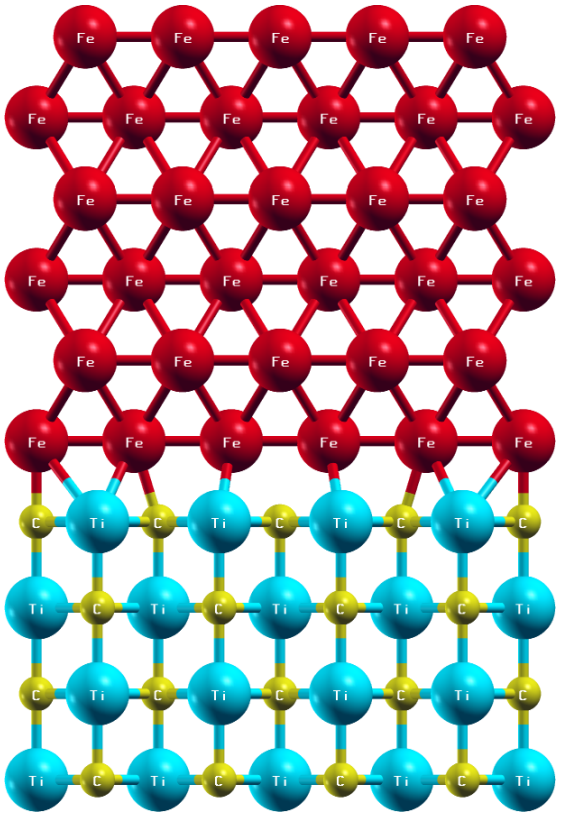
fcc Fe/MC semicoherent interface model



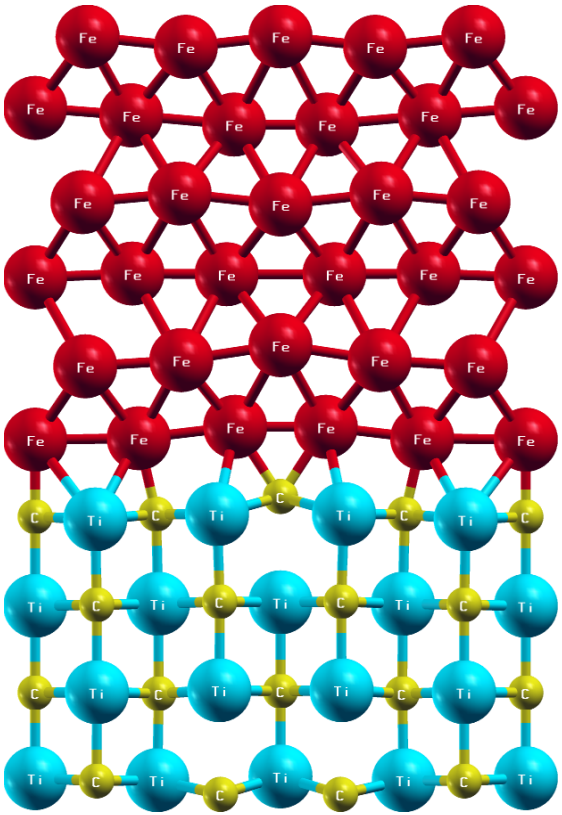
- 5 unit cells of fcc Fe matched with 4 unit cells of MC (M = Ti, V, Nb, Mo)
- Lattice misfit is eliminated or reduced dramatically
- One misfit dislocation in each unit
- Large unit cells:
  - 290 atoms if semi-coherent in [100] and [010]
  - 58 atoms if semi-coherent in [100] and coherent in [010]

fcc Fe/TiC semicoherent interface

Non-relaxed

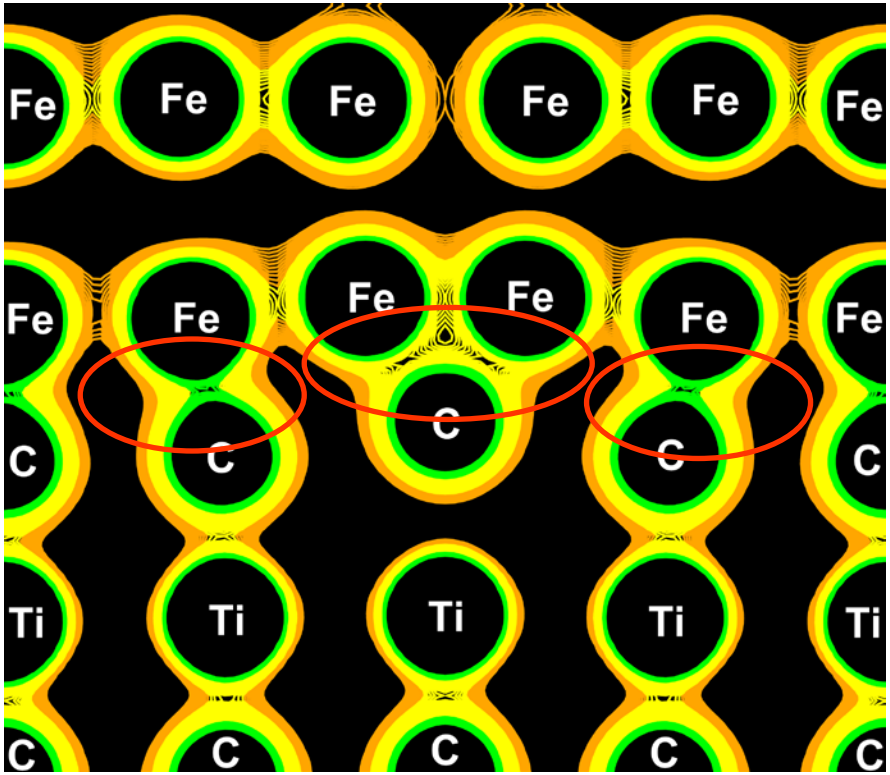


Relaxed



- **Relaxation at the interface results in formation of Fe-C bonds across the interface**

Charge density for fcc Fe/TiC semicoherent interface



- **Strong covalent bonding of Fe and C atoms at the interface**
- **Fe-C distance is 1.98 Å, compared with 1.90 Å for coherent model**
- **C atom at the end of extra plane moves to form bonds with 2 Fe atoms simultaneously**
- **In-plane relaxation rearrange Fe atoms to minimize the effect of the extra plane on the interface energetics by forming Fe-C bonds**

Conclusions

- **Strong interface adhesion is found for coherent (bcc, fcc)Fe/*M*C (M=Ti, V, Nb, Mo) interfaces, with separation energy 3.58-3.80 J/m^2**
- **High adhesion energy is due to formation of Fe-C bonding across the interface with covalent character**
- **Misfit dislocations reduce the separation energy by 20% (bcc Fe/*M*C) to 40% (fcc Fe/*M*C)**
- **Separation energy reduction correlates with lattice misfit**
- **Semicoherent interface retain adhesion and bonding due to relaxation leading to formation of new Fe-C bonds at the interface**