STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

Ab initio study of synergetic effects of Mn and Si in the interaction with point defects in bcc Fe

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UNIVERSITEIT GENT

PERFORM 60
FP7 Project

Ab initio study of synergetic effects of Mn and Si in the interaction with point defects in bcc Fe

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Introduction

Fe-Cr (7-14%) ferritic-martensitic **steels** – candidates for GEN IV and fusion installations

Advantages:

- Low swelling for operating temperatures
- Low DBTT shift during/after irradiation
- Small creep rate under influence of irradiation and temperature
- Good radiation resistance
- Good thermomechanical properties
- High corrosion resistance

Problems during operation:

- neutron radiation changes microstructure (point defect clusters, dislocation network, precipitates)
- microchemistry (segregation of alloying elements and impurities at sinks. i.e. grain boundaries)

which result in the degradation of mechanical properties:

- radiation-induced hardening
- embrittlement

The problem in mind

Chemical compositions of T91, HCM12A, HT-9 and 9Cr model alloy in at% and wt%, respectively.

		Fe	Cr	Ni	Mn	Si	C	P	Cu	V	W	Mo	S	N	Nb	Al
T91	at%	88.27	8.90	0.20	0.45	0.55	0.46	0.016	0.15	0.23	–	0.52	0.005	0.19	0.005	0.045
	wt%	89.15	8.37	0.21	0.45	0.28	0.1	0.009	0.17	0.216	–	0.9	0.003	0.048	0.008	0.022
HCM12A	at%	84.14	11.62	0.37	0.65	0.54	0.51	0.029	0.90	0.21	0.58	0.17	0.003	0.25	0.03	0.002
	wt%	84.22	10.83	0.39	0.64	0.27	0.11	0.016	1.02	0.19	1.89	0.3	0.002	0.06	0.054	0.001
HT-9	at%	83.99	12.34	0.47	0.52	0.43	0.92	0.004	0.035	0.33	0.16	0.58	0.01	0.185	–	<0.02
	wt%	85.01	11.63	0.5	0.52	0.22	0.2	0.002	0.04	0.3	0.52	1	0.006	0.047	–	<0.01
9Cr model	at%	90.42	9.24	–	–	–	0.33	<0.01	–	–	–	–	0.002	0.009	–	–
	wt%	91.24	8.68	–	–	–	0.072	0.005	–	–	–	–	0.001	0.002		

Post irradiation (doses up to 10 dpa, T=300-500 K) analysis [1-4] results have shown formation of:

- Cu-rich: ρ=(0.17-2.96)×10^{23} m-3 Ṝ=(1.7-4.5) nm
- Cr-rich precipitates: ρ=(4.6-13.4)×10^{23} m^{-3} Ṝ=(1.5-2.3) nm
- Cr-Si-Ni-P clusters: ρ=(0.4-2.9)×10^{23} m^{-3} Ṝ=(1.4-2.4) nm

Radiation-induced segregation!

- Mn-Ni-Si clusters: ρ=(0.08-2.69)×10^{23} m^{-3} Ṝ=(1.3-6.0) nm

Below the solubility limit!

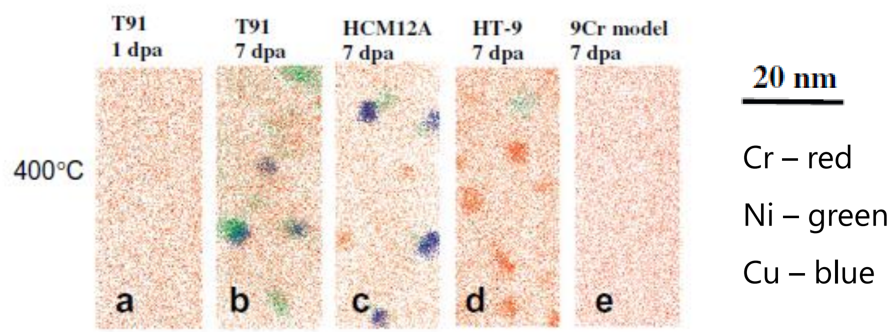
Analysis of alloy is done by:

1). scanning electron microscope (SEM)

2). transmission electron microscope (TEM)

3). atom probe tomography (APT)

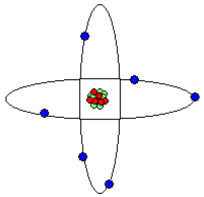
4). small angle scattering (SANS)



[1] V. Kuksenko, C. Pareige and P. Pareige, J. Nucl. Mater. 432 (2013) 160-165.
[2] V. Kuksenko, C. Pareige, C. Genevois, F. Cuvilly, M. Roussel and P. Pareige, J. Nucl. Mater. 415 (2011) 61-66.
[3] V. Kuksenko, C. Pareige and P. Pareige, J. Nucl. Mater. 425 (2012) 125-129.
[4] Z. Jiao and G.S. Was, Acta Materialia 59 (2011) 4467-4481.

Methodology. Density functional theory (DFT)

- Quantum-mechanical approach to study electronic structure
- Electron density functional for many-electron systems



Advantages	Limitations
• Accuracy • Description of complex systems • Substantial database of accumulated data	• Small systems – up to 500 atoms • CPU time ☹ • 0K calculations

Methodology. VASP parameterization

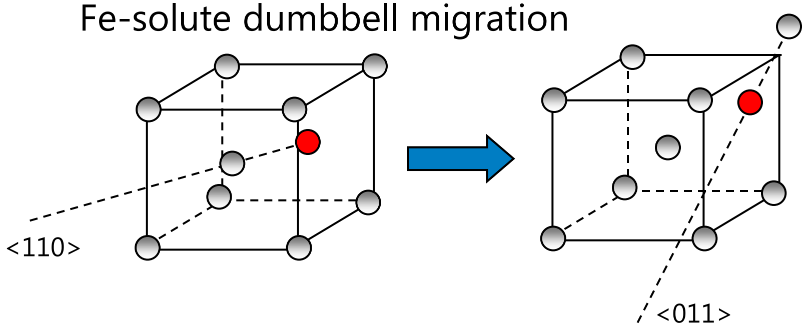
128 atoms for point defect calculations

- PAW potential generated with GGA-PW91
- 3x3x3 k-point mesh
- 300 eV cut-off energy
- Constant volume
- Relaxation criterion: ionic relaxation stops if all forces on all nuclei are smaller than 0.03 eV/Å
- Antiferromagnetic spin of Mn

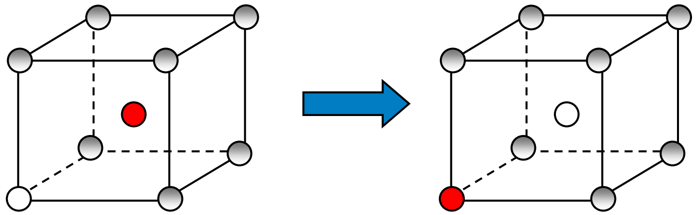
Interaction energy: $E_i = E(\Sigma A_i) + (n-1)E_0 - \Sigma E(A_i)$ if negative=attraction

Recent studies

Fe-solute dumbbell migration

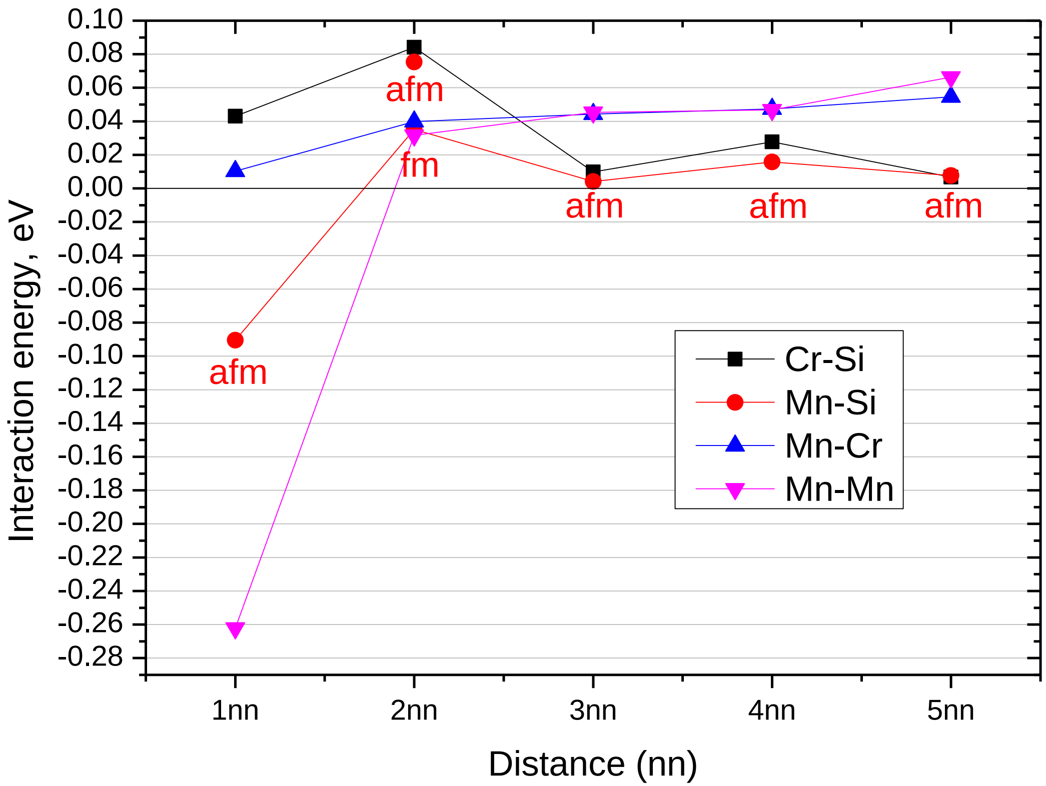


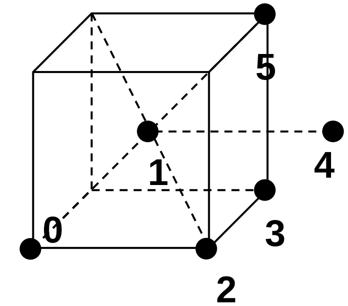
Solute-vacancy exchange



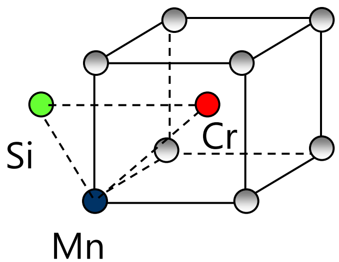
[1] O.I. Gorbatov, P.A. Korzhavyi, A.V. Ruban, B. Johansson and Y.N. Gornostyrev, J. Nucl. Mater. 419 (2011) 248-255.

Results. Solute-solute interaction





Nearest neighbour positions in bcc



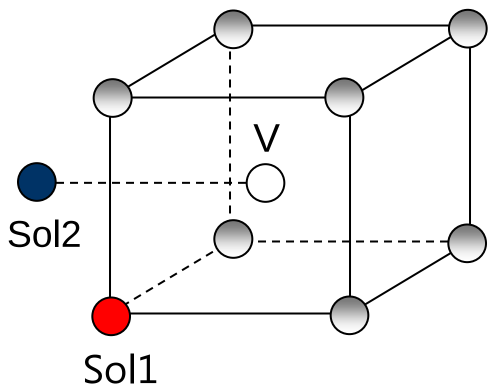
E_i(Mn-Ni-Cr) = +0.06 eV

Mn-Si pair (1nn) is the stable cross-pair

Results. Interaction of Mn-Si and vacancy

E_i(Mn-Si)=-0.09 eV

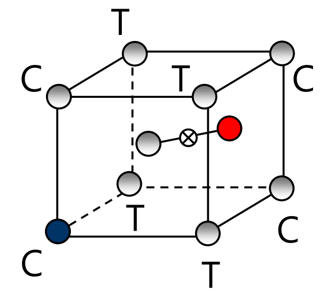
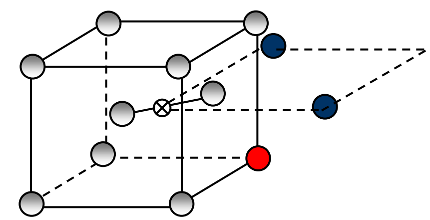
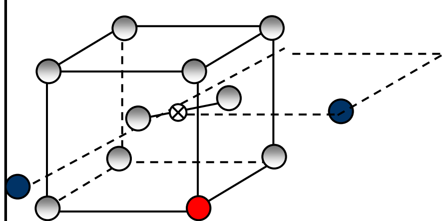
Configuration: Vacancy + S1 + S2	E_I(vacancy-MnSi), eV	E_I(vacancy-S1), eV	**Δ*E*, eV**
Vac+Si(1nn)+Mn	-0.34	-0.31	-0.03
Vac+Mn(1nn)+Si	-0.25	-0.17	-0.08



There is no sinergy of Mn-Si in interaction with vacancies;

the vacancy increases the binding Mn-Si by 0.25-0.34 eV

Results. Interaction of Mn-Si and Fe-Fe dumbbell

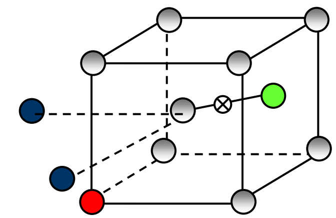
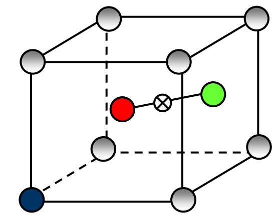
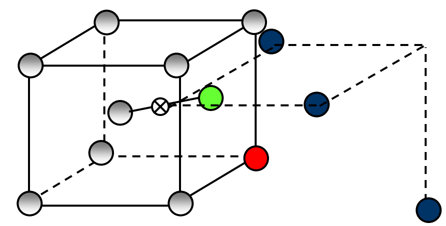
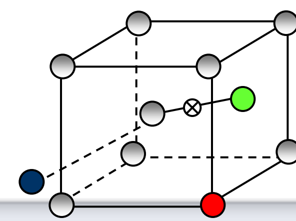
Configuration: point defect + S1 + S2	E_I(PD-S1&S2), eV	E_I(PD-S1), eV	**Δ*E*,** eV	Equivalent positions of the S2, see Fig.1.
FeMn+Si	-0.78	-0.59	-0.19 **Enhanced!**	
FeSi+Mn	-0.42	0.00 **Not stable**	-0.42	
FeFe+Mn(C)+Si	-0.39	-0.32	-0.07	
FeFe+Si(C)+Mn	-0.37	-0.28	-0.09	
FeFe+Mn(T)+Si	-0.17	-0.09	-0.08	

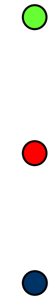
● Sol1

● Sol2

Mn and Si show sinergetic effect while interacting with Fe-Fe dumbbell; Fe-Fe dumbbells raise E_i(Mn-Si) by 0.17-0.39 eV.

Results. Interaction of Mn-Si and Fe-Cr dumbbell

Configuration: point defect + S1 + S2	E_I(PD-S1&S2), eV	E_I(PD-S1), eV	**Δ*E*,** eV	Equivalent positions of the S2, see Fig.1.
FeCr+Si(C2)+Mn	-0.41	-0.30	-0.11	
FeCr+Mn(C2)+Si	-0.40	-0.30	-0.10	
MnCr+Si	-0.29	-0.24	-0.05	
FeCr+Mn(C1)+Si	-0.09	-0.12	0.03	
FeCr+Mn(T)+Si	-0.08	-0.01	-0.07	



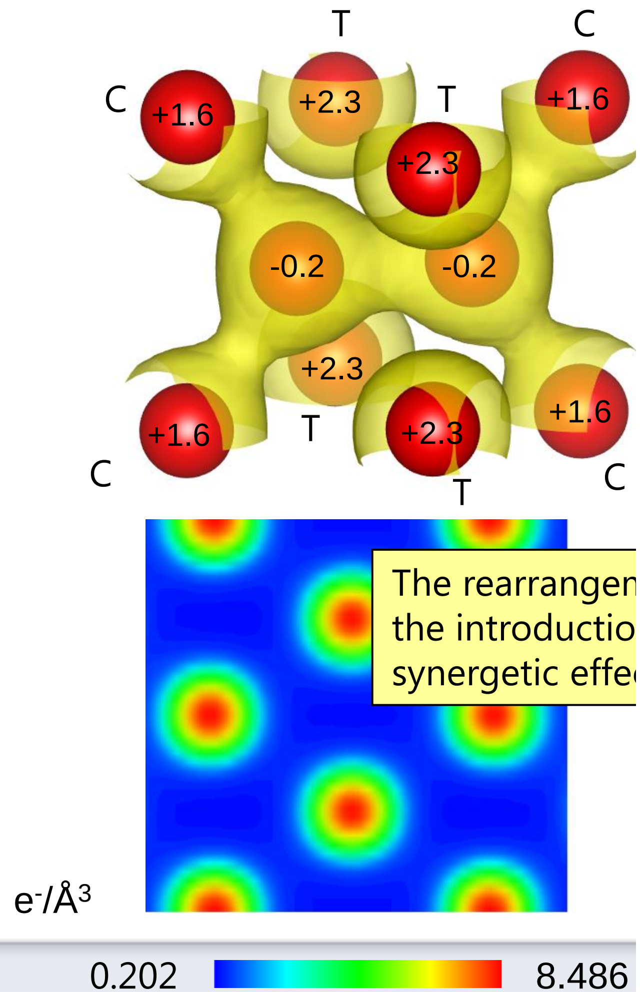
No sinergy of Mn and Si while interacting with Fe-Cr dumbbell.

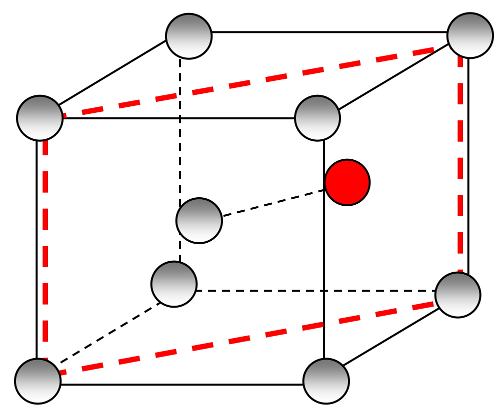
Fe-Cr enhances Mn-Si attraction by 0.08-0.41 eV.

Results. Reasons of sinergetic effect

Fe-Fe dumbbell

Isosurfaces of 0.55 $e^{-}/Å^{3}$





Summary

In FeCr-Mn-Si system:

- Mn-Si (1nn) – weakly attractive pair (E_i=-0.09 eV). Mn-Si-Cr clusters are not likely to be formed
- Mn-Si binding is enhanced in the presence of vacancies (by up to 0.34 eV), Fe-Fe (by up to 0.39 eV) and Fe-Cr dumbbells by up to 0.41 eV
- The interaction energy of the Mn-Si solute clusters with a single vacancy is linearly additive
- A considerable synergetic effect in the case of self-interstitial atoms bound to Mn-Si pairs has been established. Sinergy of Mn and Si on stability Fe-Fe is likely to originate from compensation of magnetic moments. It can be present even without Cr
- Mn-Si enriched clusters may originate from the nucleation and growth of point defect clusters at Mn-Si pairs, acting as configurational traps immobilizing SIAs

Questions?

Thank you for your attention

Atomic modelling team

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