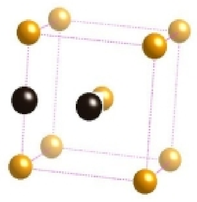

Fe and B Substituted $Cr_{23}C_6$ using First-principles Study

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$Cr_{23}C_6$ and its various solid solutions are vital phases in the most modern creep-resistant steels. Although there has been a great deal of work in understanding the significance of this carbide with respect to elevated temperature properties, the detailed thermodynamic properties deserve further attention. In particular, there is a long-term need to establish the atom-distribution, energetic and structural implications of different atoms in the basic $Cr_{23}C_6$ crystal structure, including solutes such as iron and boron. The standard thermodynamic assessments which are based on macroscopic measurements have not revealed such information. To work towards this goal, we use the all-electron full potential linearized augmented plane-wave method (FLAPW) within the generalized gradient approximation, a scheme more accurate than a variety of other density functional methods. The calculated ground state equilibrium lattice parameter is 10.57 Å for nonmagnetic $Cr_{23}C_6$ and 10.56 Å for ferromagnetic $FeCr_{22}C_6$ where the Fe atom prefers to substitute on the "4a" site. The formation enthalpy of $Cr_{23}C_6$ is calculated to be 1.82 kJ atom-mol^{-1} higher than the lowest formation enthalpy of $FeCr_{22}C_6$. In future work we hope to introduce boron and nitrogen into the lattice given its known influence on the coarsening behavior of the carbide, and indeed to incorporate the energies thus calculated into phase diagram calculation methods such as CALPHAD.

Creep Resistant Steels

Creep-resistant steels are mainly used in power plant applications to increase the economic efficiency.

Steam Power Plant Efficiency

Current ~ 42 %

600 °C
30 MPa

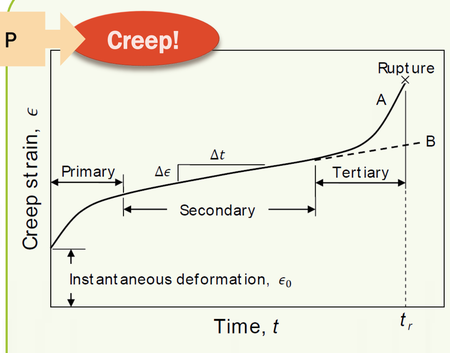
650 °C
120 MPa

Goal ~ 45 %

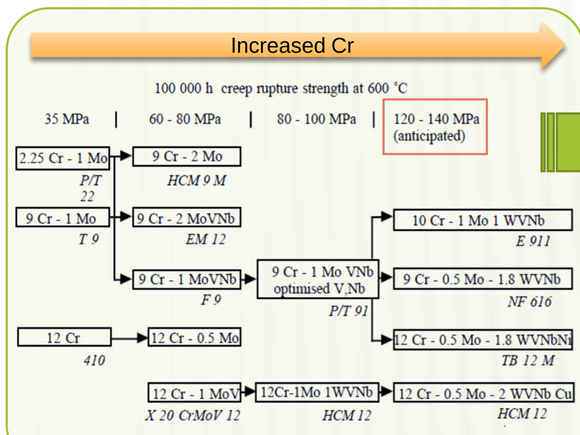
Control Measure	Increase in Efficiency / %
Reduction of condenser pressure by 50 %	1.5
60 °C increase in steam temperature	1.4
Use of double reheat	1
20 % increase in steam pressure	0.3
Reducing excess air by 10 %	0.25
10 °C decrease in flue gas temperature	0.25

Anticipated efficiency improvements for changes in power plant operating conditions [Wachter and Ennis, 1995]

High T, P → **Creep!**



Typical creep curve at constant load A and constant stress B at constant elevated temperature. [Callister, 2007; Dieter, 1998]



Development of 9 to 12 wt% Cr Steels [Wachter and Ennis, 1995]

Aim of the Study

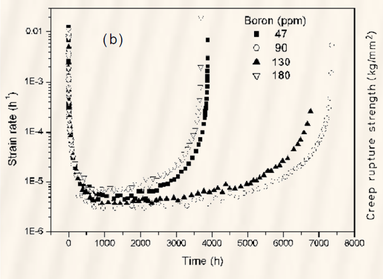
Understanding the role of B in influencing the stability of $M_{23}C_6$

1. Thermodynamic Stability
- B dissolves in $M_{23}C_6$
- B segregates to α/ $M_{23}C_6$ interface

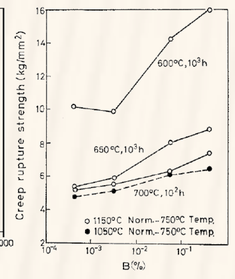
Calculate formation enthalpy of $M_{23}C_6$ with B
Calculate the new phase diagram at high T

Influence of Boron

Boron containing steel
- Retards the transition from secondary to tertiary creep
- Increases the creep rupture strength



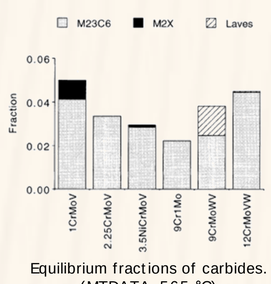
Influence of B on 9Cr3W3CoNbV steel at 650 °C at 100 MPa. [Albert *et al.*, 2005]



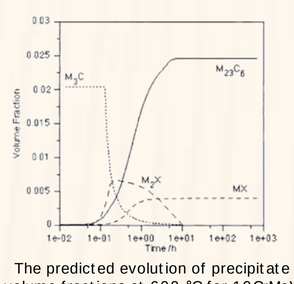
9Cr-1Mo-V-Nb with addition of B. [Mimino *et al.*, 1978]

$M_{23}C_6$ Carbides

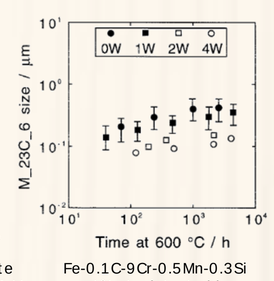
In creep-resistant steels, in equilibrium after creep
- $M_{23}C_6$ is the majority carbide.
- $M_{23}C_6$ coarsens



Equilibrium fractions of carbides. (MTDATA, 565 °C) [Bhadeshia, 2001]



The predicted evolution of precipitate volume fractions at 600 °C for 10CrMoV [Robson and Bhadeshia, 1997]

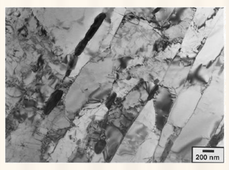


Fe-0.1C-9Cr-0.5Mn-0.3Si wt% steel, tested in creep at 600 °C [Abe].

B in $M_{23}C_6$

Verified the boron distributed evenly within $M_{23}C_6$ in ferritic creep-resistant steels.

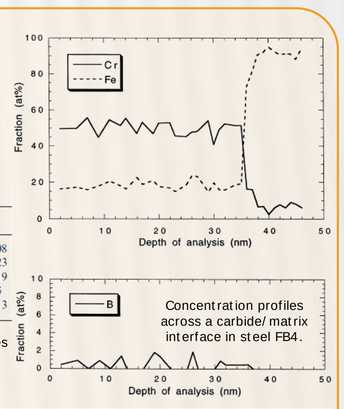
[Hättestrand and Andrén, 1999]



Martenstitic 9-12% Cr steel in the tempered condition. (TEM)

	Fe	Cr	B
FB4	18.8 ± 0.5	50.4 ± 0.8	0.50 ± 0.08
CB1	18.1 ± 0.9	47.4 ± 1.2	0.99 ± 0.23
CB1	19.4 ± 1.0	50.4 ± 1.3	0.52 ± 0.19
CB2	17.5 ± 1.3	51.5 ± 1.9	1.8 ± 0.5
CD2	17.4 ± 0.9	50.2 ± 1.3	0.41 ± 0.13

APFIM analyses of $M_{23}C_6$ carbides (at%).



Chemical composition of investigated steels (wt. %)

	Fe	Cr	Mn	Ni	Co	Mo	W	V	Nb	C	B	N
CD2	bal.	9.5	0.9	0.1	1.0	0.5	1.8	0.21	0.04	0.06	0.004	0.05

Boron increase the creep resistance.

Boron is mostly dissolved in $M_{23}C_6$.

Need to understand the role of boron in $M_{23}C_6$ together which benefits the creep resistance.

Calculation Method

FLAPW method
Generalized Gradient Approximation
Calculated Systems
$Cr_{23}C_6$ $Fe_{23}C_6$ $Cr_{23}B_6$ $Fe_{23}B_6$ $Cr_{23}C_5B$
$Fe^{4a}Cr_{22}C_6$ $Fe^{8c}Cr_{22}C_6$ $Fe^{32f}Cr_{22}C_6$ $Fe^{48h}Cr_{22}C_6$

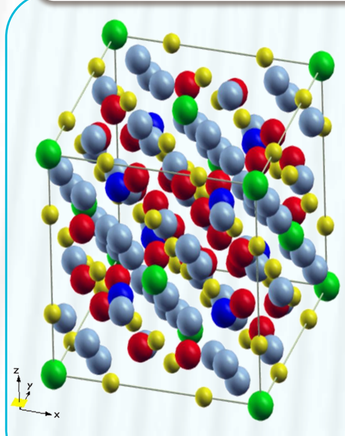
Calculated energies are at 0 K and zero pressure
ΔH_f : Formation enthalpy per atom of $Cr_xFe_yC_pB_q$
E(X) : Calculated ground state energy of X
N : Number of atoms, x+y+p+q

$$\Delta H_f(Cr_xFe_yC_pB_q) = \{E(Cr_xFe_yC_pB_q) - xE(Cr) - yE(Fe) - pE(C) - qE(B)\}/N$$

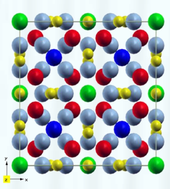
E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, *Phys. Rev. B* **28** (1981).
M. Weinert, E. Wimmer, and A. J. Freeman, *Phys. Rev. B* **26** (1982).
Perdew, J. P., Burke, K., Ernzerhof, M., *Phys. Rev. Let.* **77** (1996).
S-W Seo, YY Song, G. Rahman, IG Kim, M Weinert, and AJ Freeman, *J. Magnetics* **14** (2009).

Crystal Structure

$Fm\bar{3}m$



$Cr_{23}C_6$ unit cell

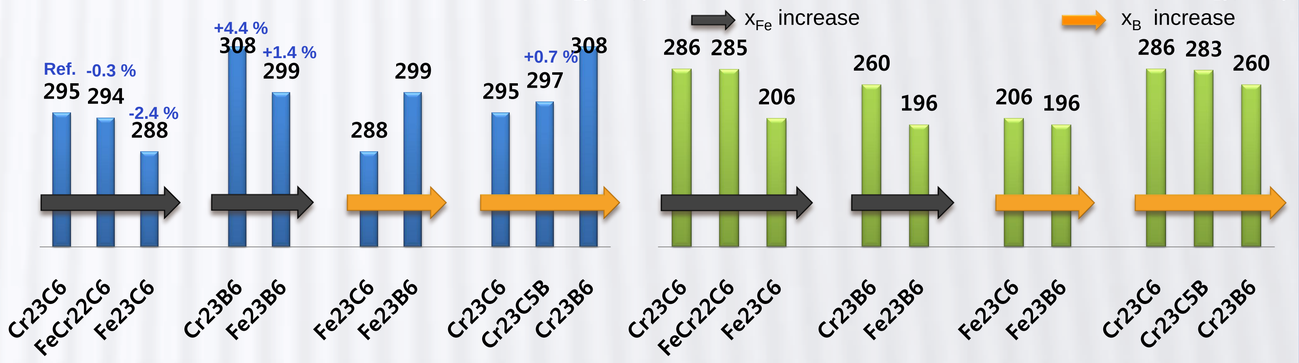


[100] projection of $Cr_{23}C_6$

Calculated Volume and Bulk Modulus of $M_{23}C_6$

Fe decreases, B increases the volume of the unit cell of $M_{23}(B,C)_6$

Fe and B decreases the bulk modulus of the unit cell of $M_{23}(B,C)_6$

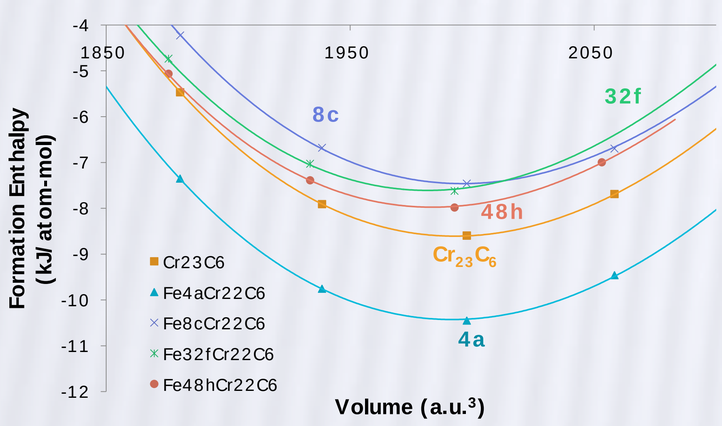


Calculated volume(Å^3) of $M_{23}(B,C)_6$ unit cell

Calculated bulk modulus(GPa) of $M_{23}(B,C)_6$

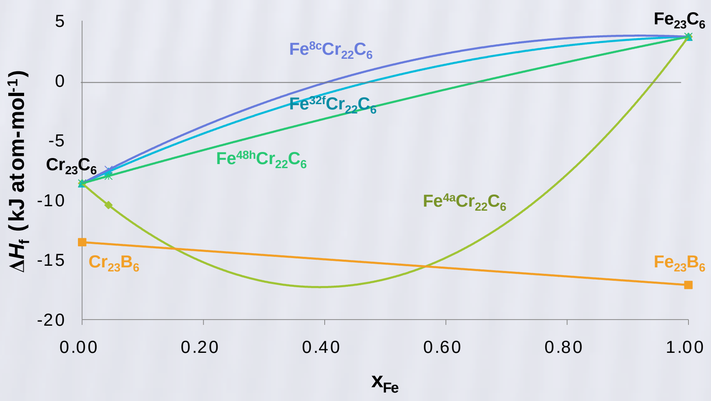
Formation Enthalpy - Fe substituted $M_{23}C_6$

Fe prefers to substitute to Cr(4a) site of $M_{23}C_6$
Fe stabilizes $Cr_{23}C_6$ when substituted to Cr(4a) site



Calculated formation enthalpy of $FeCr_{22}C_6$

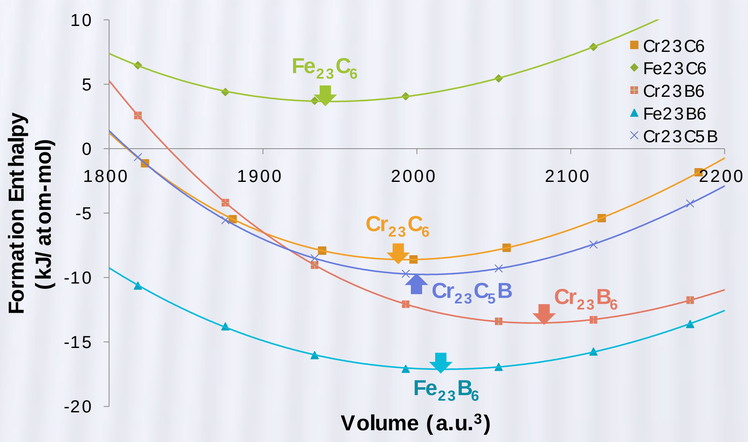
Up to 7 atoms of Fe substitution to $Cr_{23}C_6$ is stable



Calculated formation enthalpy with respect to Fe concentration

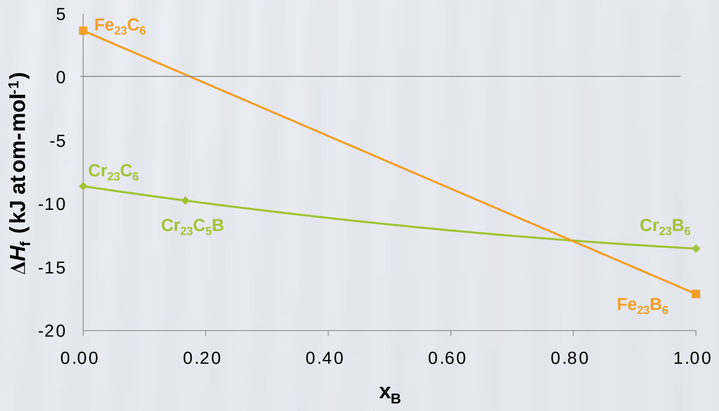
Formation Enthalpy - B substituted $M_{23}C_6$

B substitutes to C(24e) site of $M_{23}C_6$
B stabilizes $M_{23}C_6$ and increases the equilibrium volume



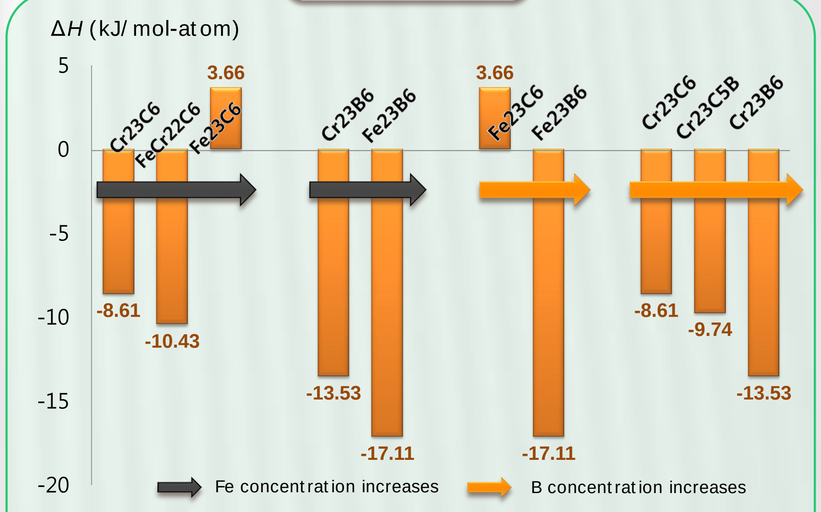
Calculated formation enthalpy of $M_{23}(C,B)_6$

B stabilizes the $M_{23}C_6$ by substituting to C site



Calculated formation enthalpy with respect to Fe concentration

Summary



Calculated formation enthalpy of $M_{23}(C,B)_6$

	a / Å	B / Gpa	ΔH_f / kJ atom^{-1} mol^{-1}	References
$Cr_{23}C_6$	10.66		-10.98	* Yakel, 1987
	10.90	275	-8.18	Xie *et al.*, 2005
	10.56	294	-9.65	Henriksson *et al.*, 2008
	10.53	298	-8.75	Chao, 2008
$FeCr_{22}C_6$	10.65			* Villars and Calvert, 1991
	10.90	278		Xie *et al.*, 2005
$Fe^{4a}Cr_{22}C_6$	10.55		-10.65	Henriksson *et al.*, 2008
$Fe_{23}C_6$			11.98	* Guillermet and Grimvall, 1992
	10.63	276	4.39	Xie *et al.*, 2006
$Fe_{23}B_6$	10.62			Ohodnicki, 2008

Lattice parameter, bulk modulus and formation energy of $M_{23}(C,B)_6$ from literatures

First consistent calculations on $M_{23}(C,B)_6$
Calculated enthalpies will be implemented to database