The magnetic-field-induced alloy element concentration change in alloy carbides

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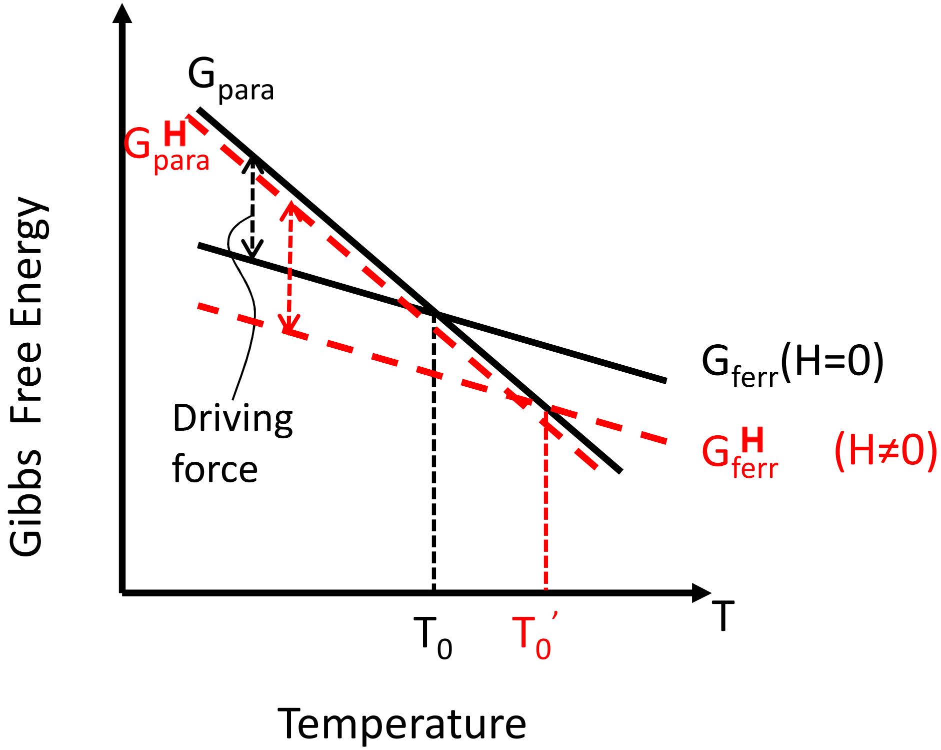
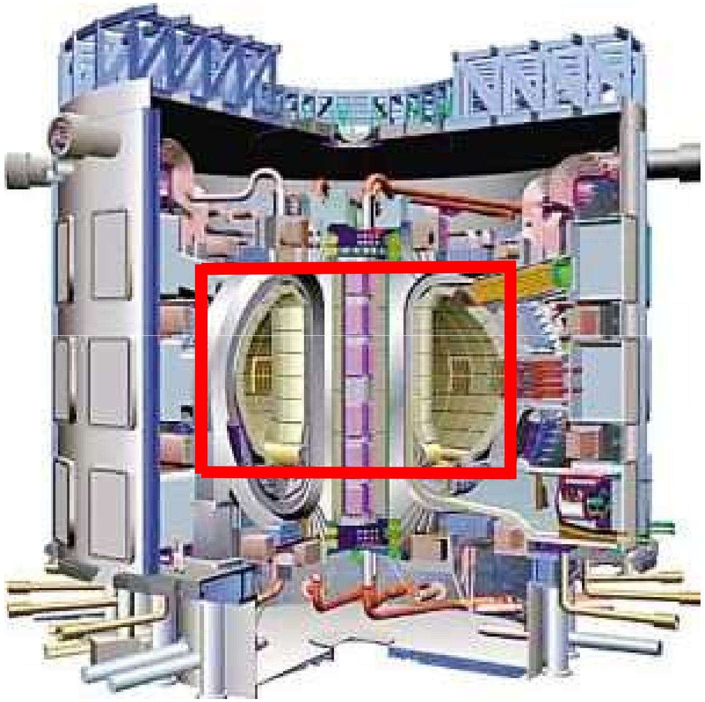
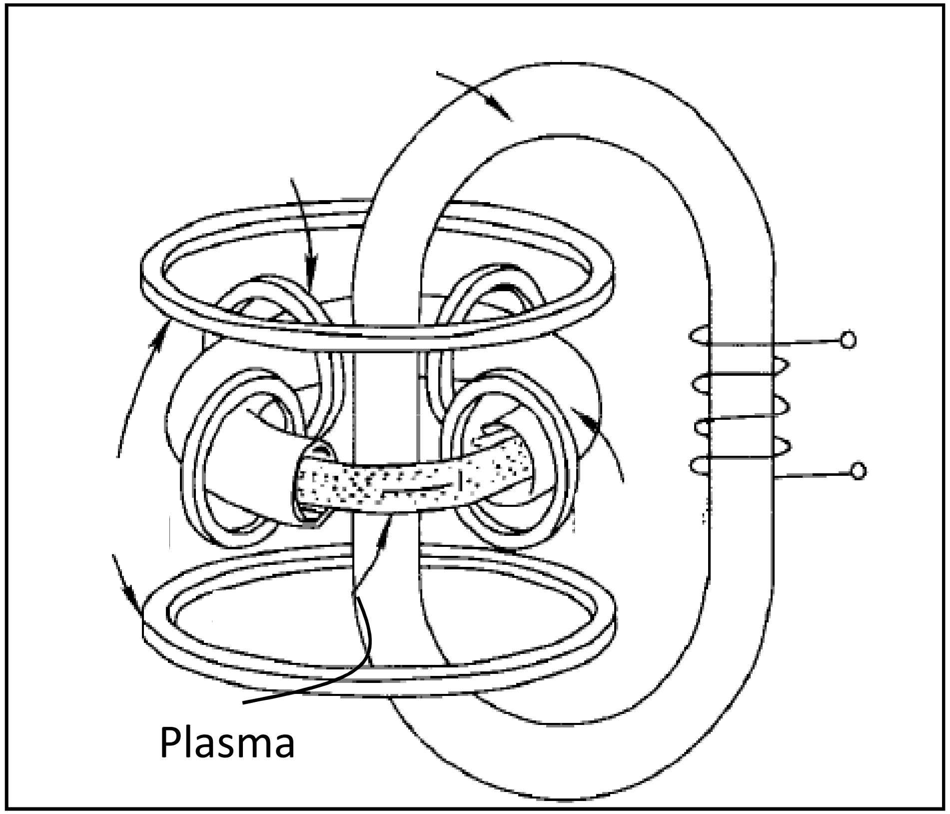
Influence of magnetic field on phase transformation



Motivation

3-5 T, 400-550 °C





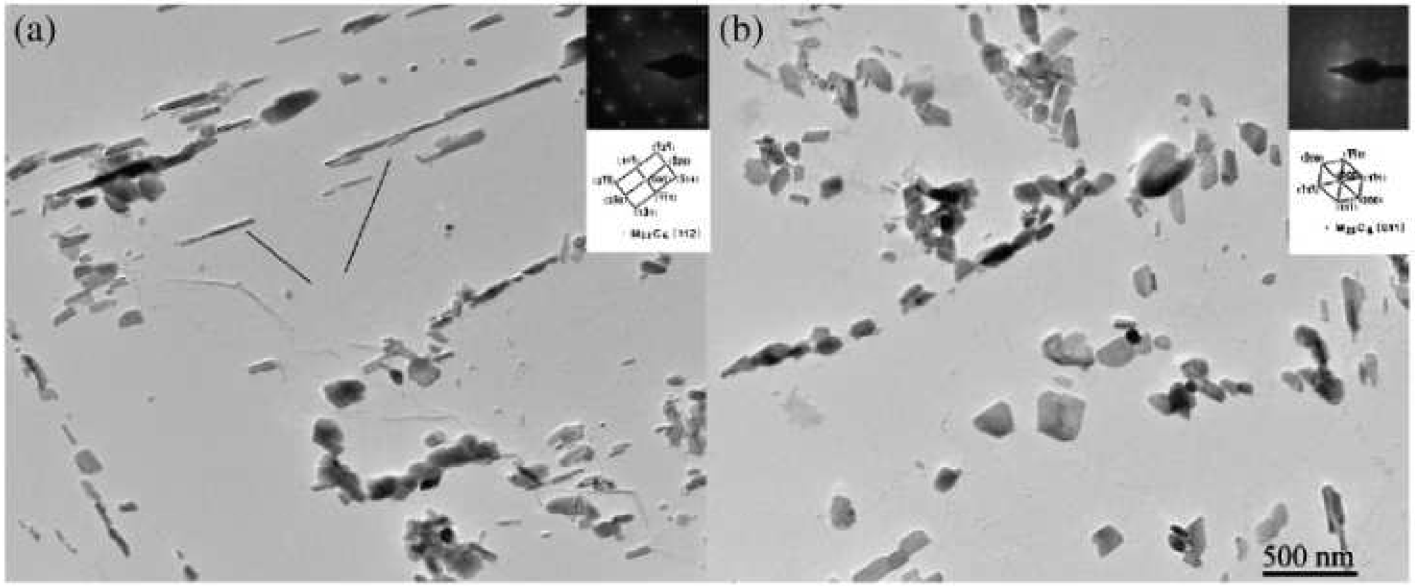
The schematic diagram of the principle component

in Tokamak in reduced activation steel

Reece, R. J. 1988

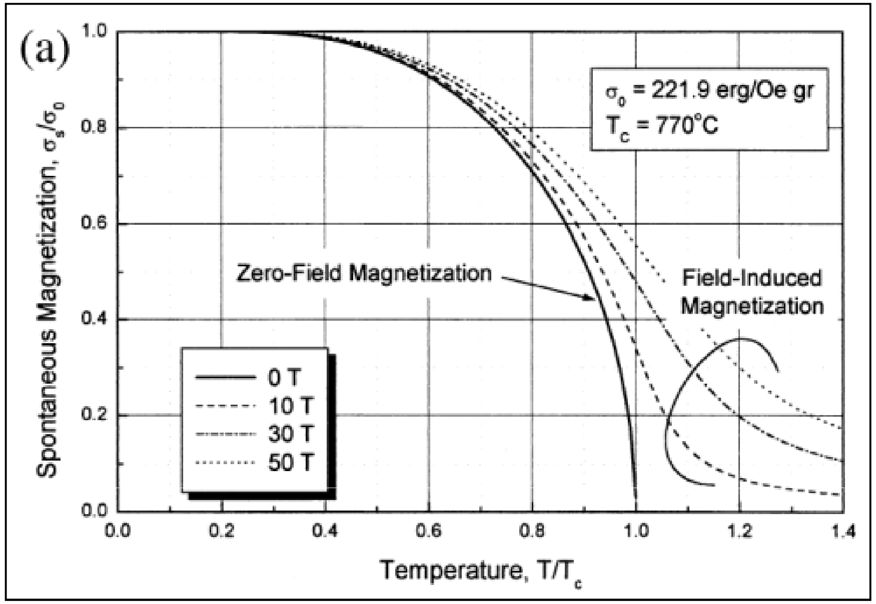
Nuclear fusion reactor

Background



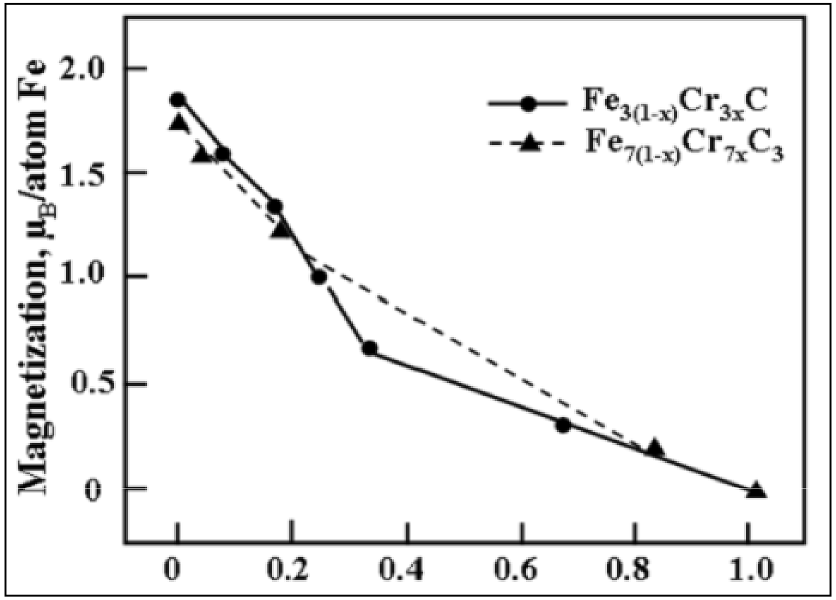
Z.X. Xia, C. Zhang *, H. Lan, Z.Q. Liu, Z.G. Yang Materials Letters 65 (2011) 937–939

The magnetic parameter of alloy carbide



The calculated variation of relative spontaneous magnetization of pure iron with relative temperature.

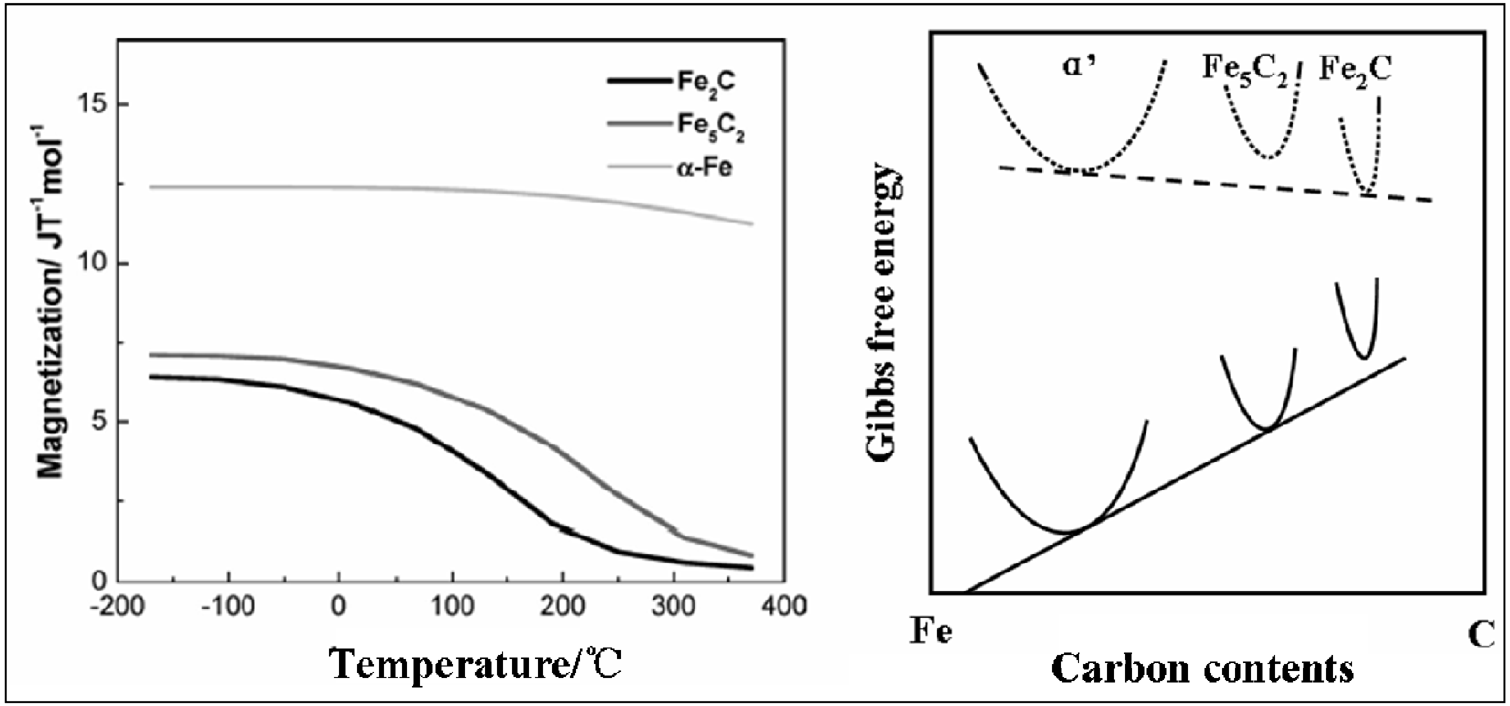
Choi J K et al. 2000



Dependences of the magnetization on the chromium concentration x in $Fe_{3(1-x)}Cr_{3x}C$ and $Fe_{7(1-x)}Cr_{7}xC_{3}$.

Konyaeva MA et al. 2009

The magnetic parameter of carbide



(a) Variations of magnetization with temperature (b) schematic diagram of Gibbs free energy with carbon concentration for Fe_2C, Fe_5C_2 and α-Fe

Y D Zhang et al. ISIJ International (2005)

Heat Treatment Equipment

Fe-0.28C-3.0Mo alloy, isothermal heat treatment

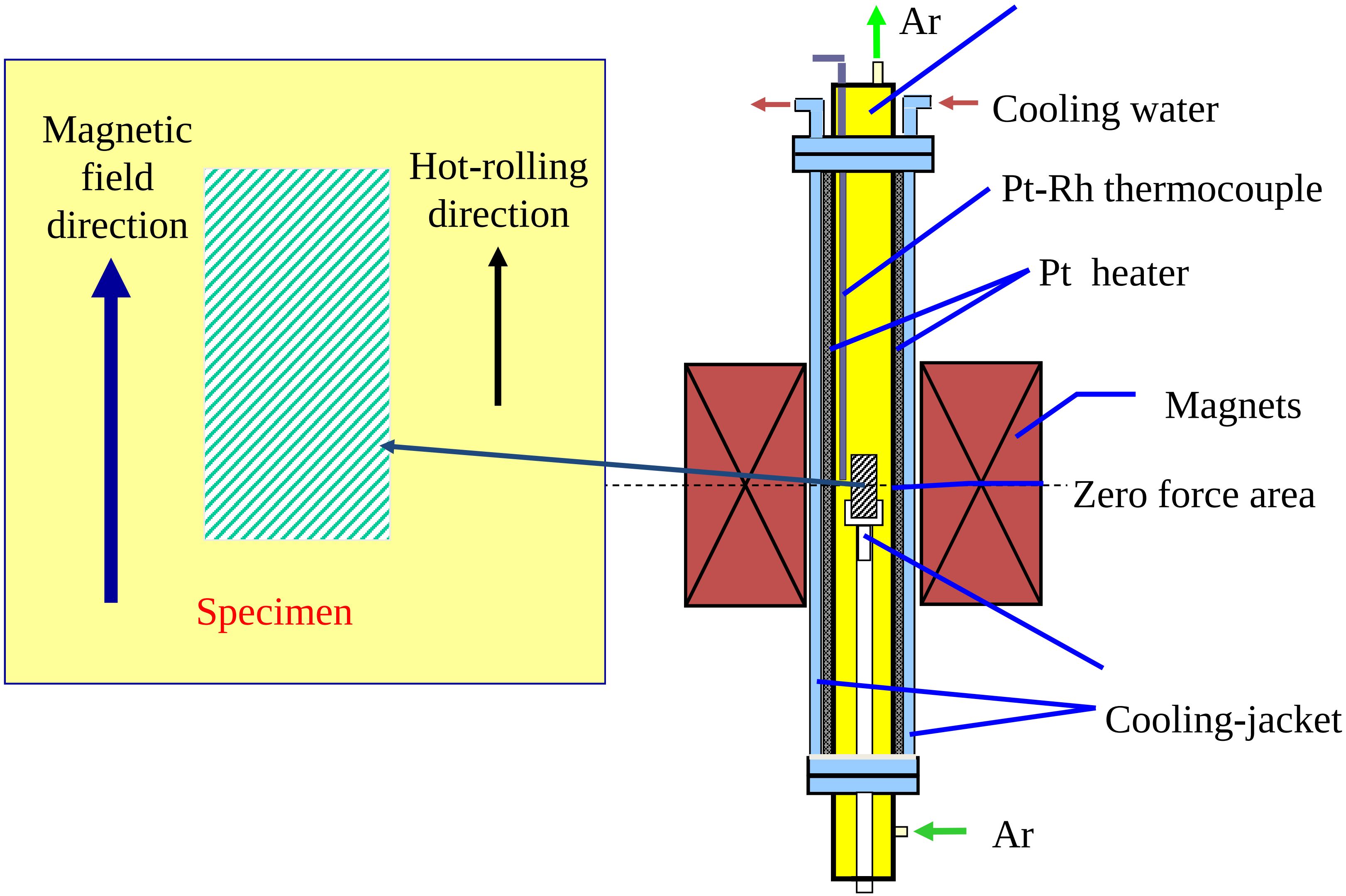
Fe-0.28C-3.0Mo alloy, temperature heat treatment

2.25Cr-1.0Mo alloy, temperature heat treatment

0 T

12 T

Heat Treatment Equipment



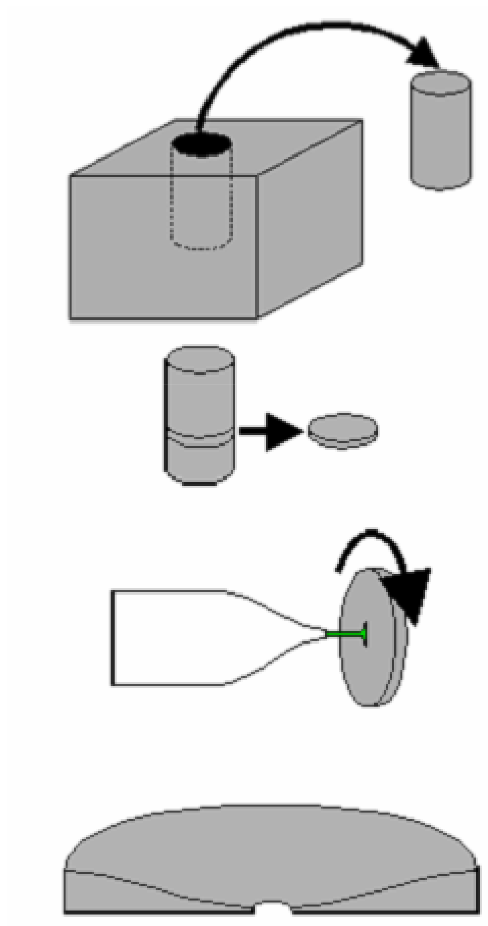
Foil and extraction Replicas (C or Au)

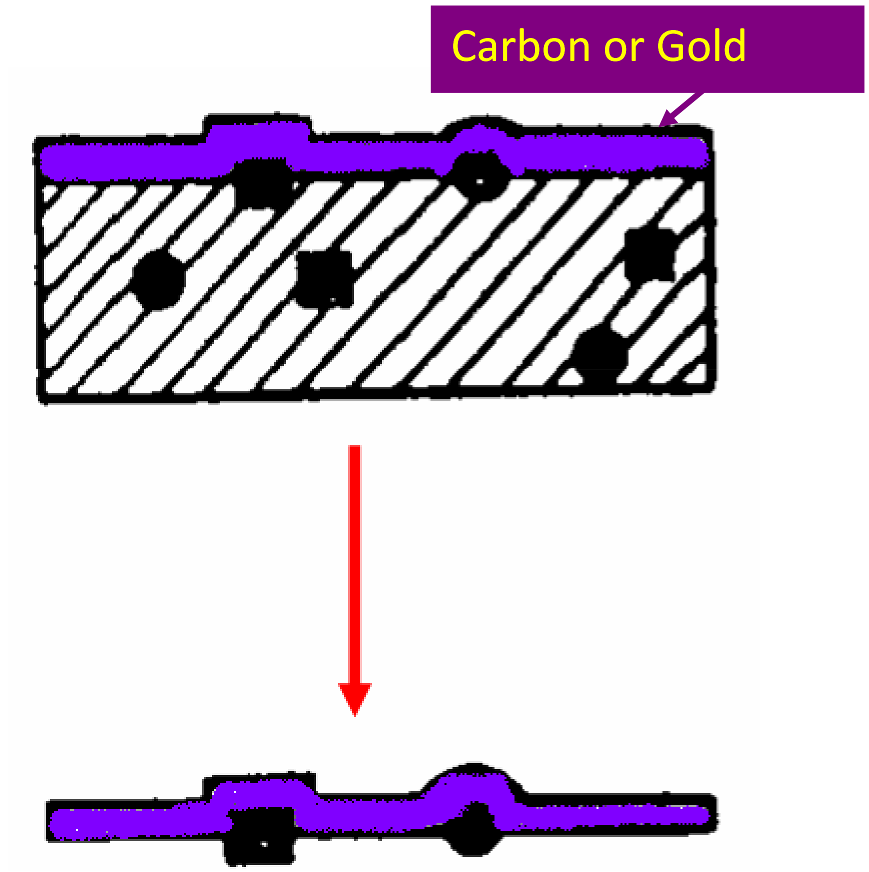
Cutting

Thin discs

Jet-polishing

Transparent

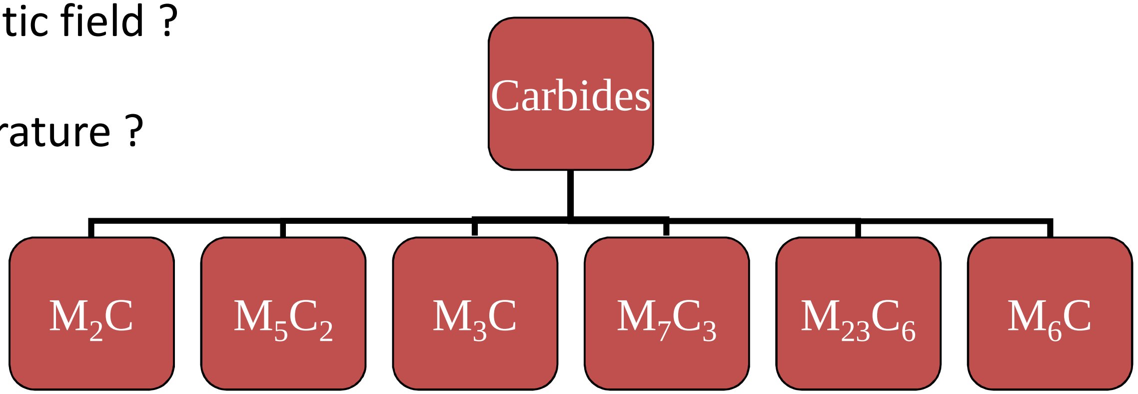




Carbides in steel

Magnetic field ?

Temperature ?



A magnetic field is usually considered to have a significant influence on ferromagnetic materials, such as alloy carbides. But less attention has been paid to alloy carbide precipitation.

Weiss molecular theory

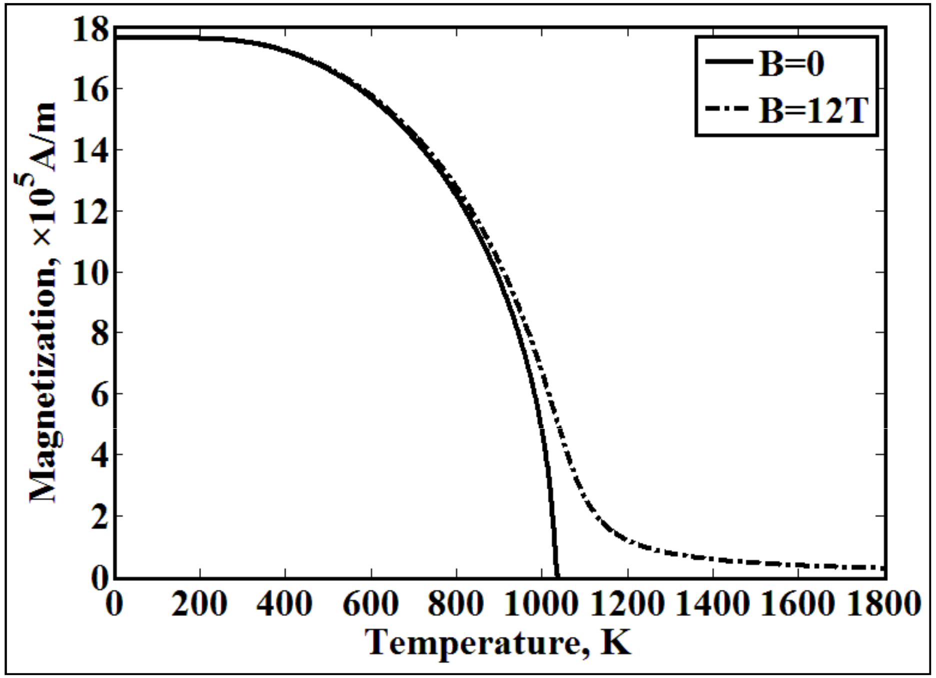
$$B = B_0 + \lambda M$$

$$B_j(\alpha) = \left\{ \frac{2j+1}{2j} cth \frac{(2j+1)a_j}{2j} - \frac{1}{2j} cth(\frac{a_j}{2j}) \right\}$$

$$T_c = \frac{(j+1) N n_B^2 \mu_B^2 \lambda}{3jk}$$

$$\alpha_j = \frac{n_B \mu_B B}{kT}$$

$$\boxed{M = NmB_j(\alpha)}$$

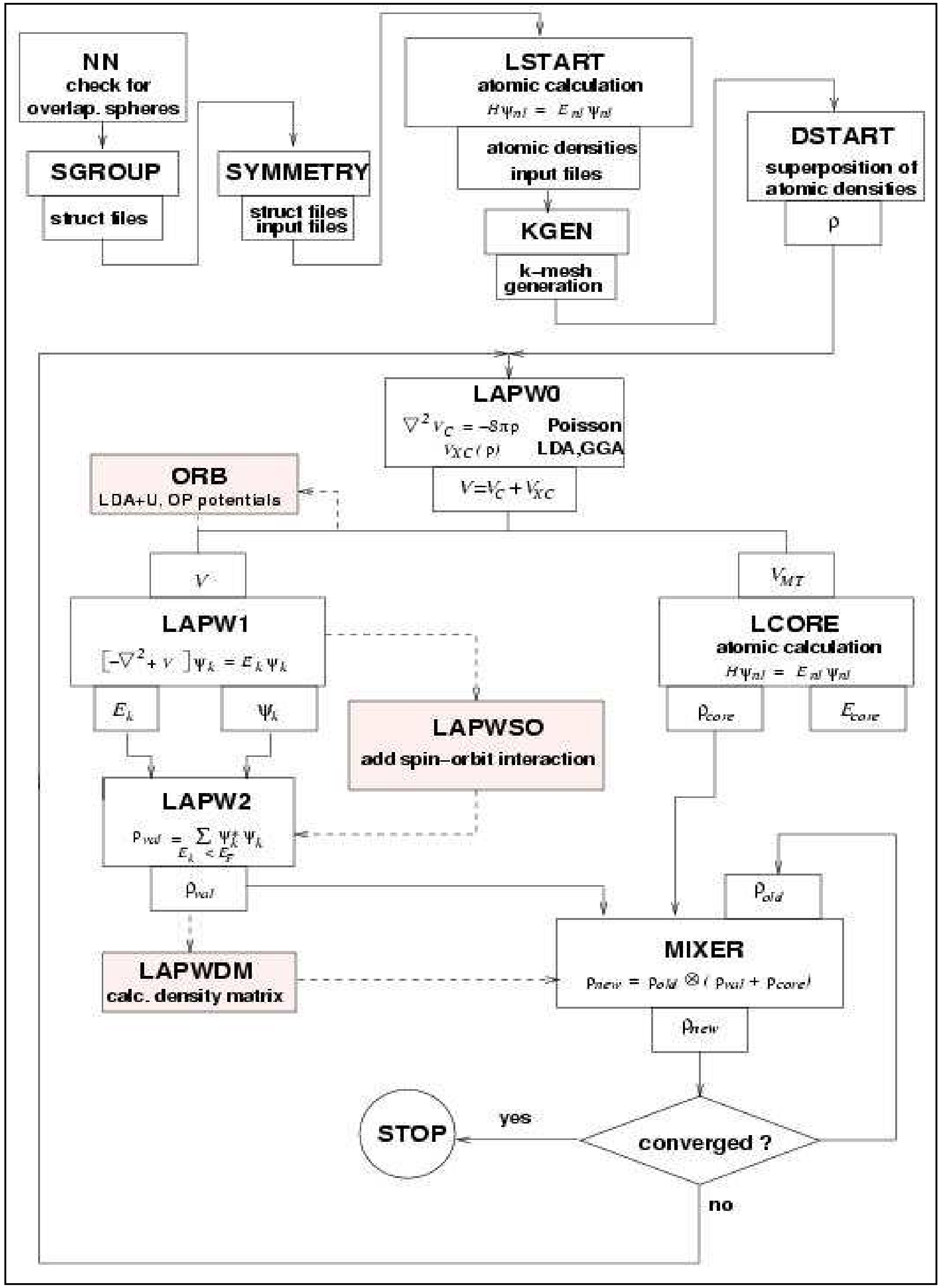


The magnetization as a function of the temperature without and with a 12-T magnetic field for pure iron

First principle calculation

Program structure of WIEN2k

The all-electron FPLAPW method was used as embodied in the WIEN2K code. The exchange-correlation potential was calculated using the GGA via the scheme of Perdew-Burke-Ernzerhof 96 (PBE-GGA)



Part Ⅰ

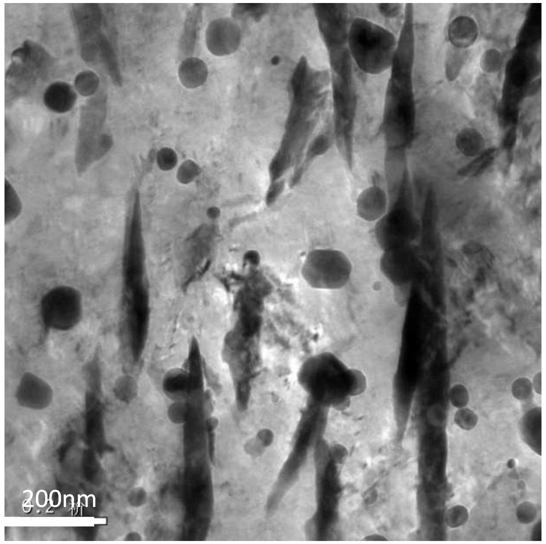
The influence of the high magnetic field on the alloy carbide in austenite-ferrite isothermal transformation of Fe-C-Mo alloy

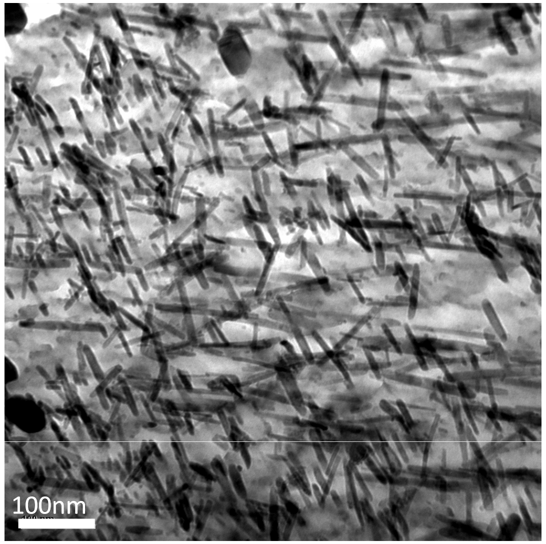
Different morphology of carbides

Irregular

M_3C (including Fe_3C)

610-20s-off





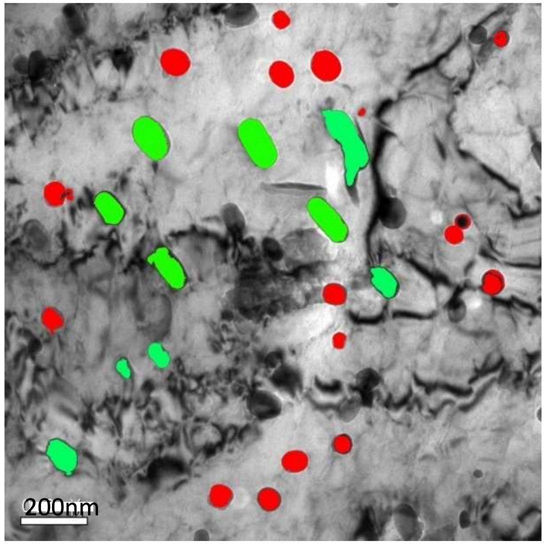
Lath or needle

M_2C

700-3600s-on

Rod M_6C

530-60s-on



Spheroidal M_6C

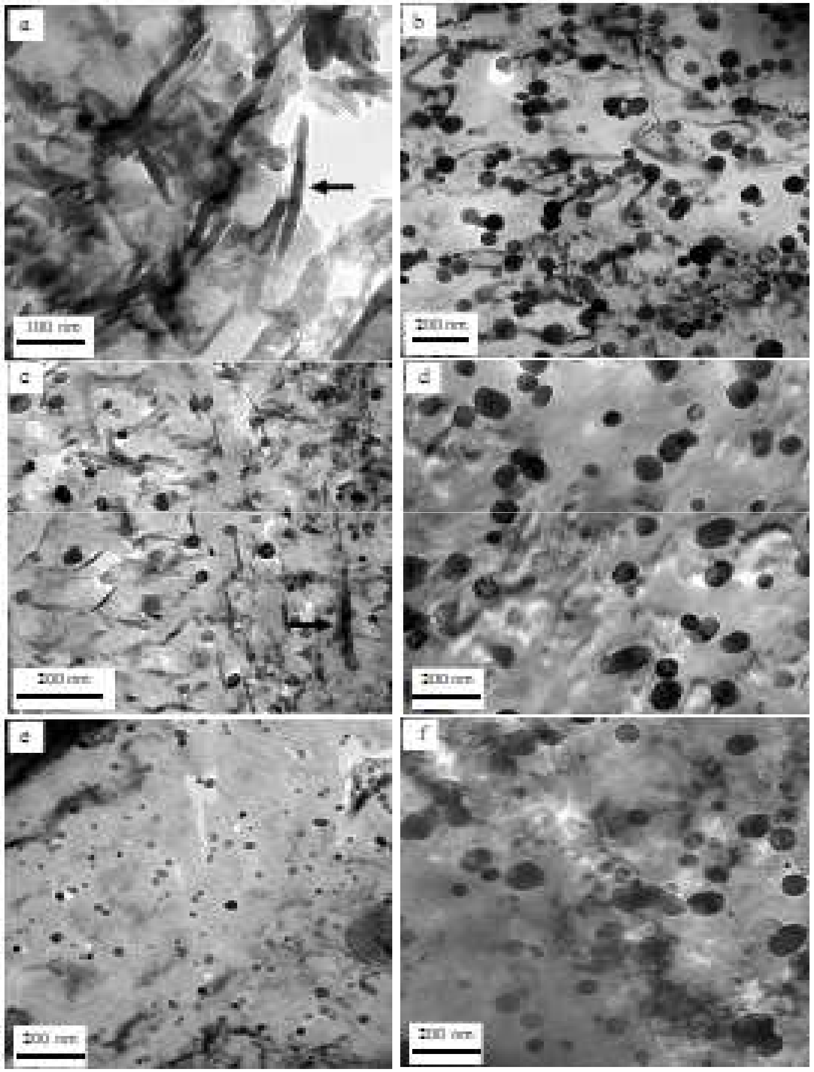
Morphology of carbides at 530-610 °C

0 T

20s

60s

600s



20s M_6C

60s M_6C

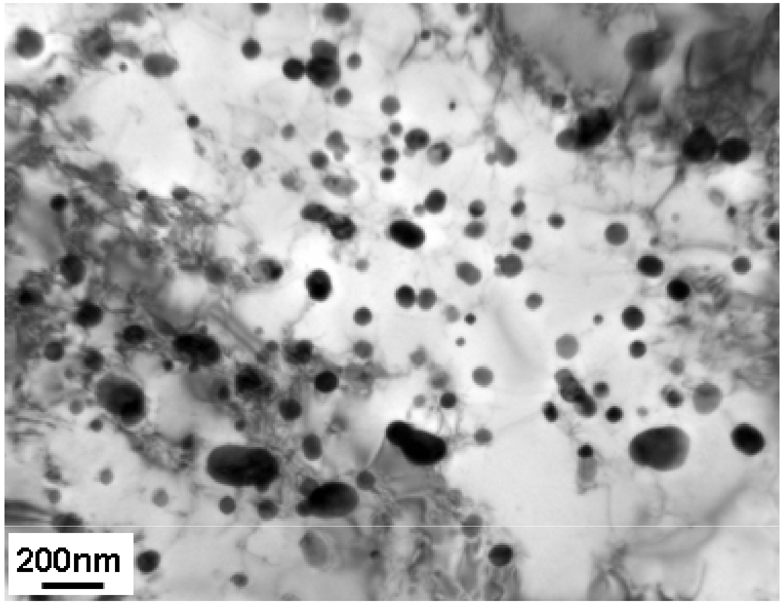
600s M_6C

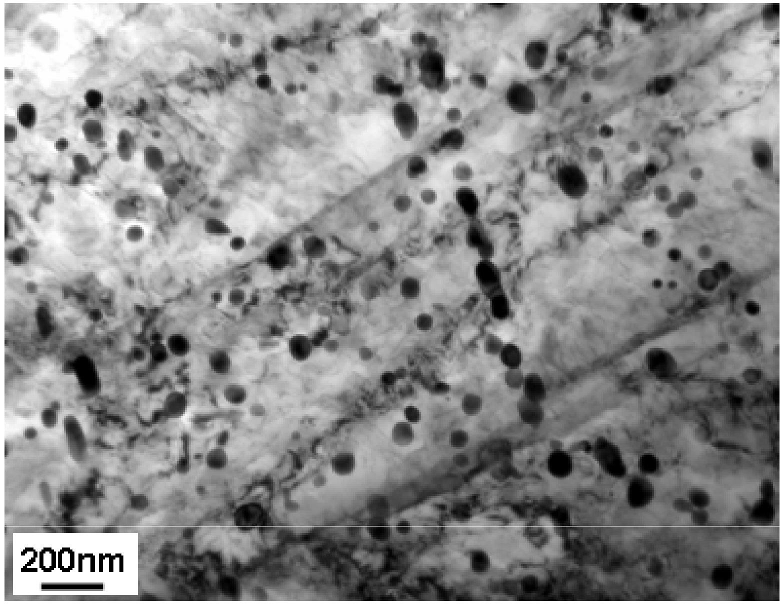
12 T

Magnetic Field promotes the precipitation of M_6C

Magnetic Field promotes the precipitation of M_6C

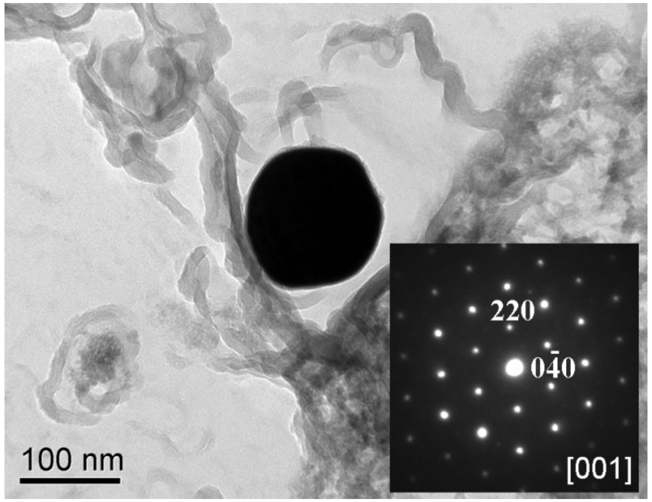
0 T



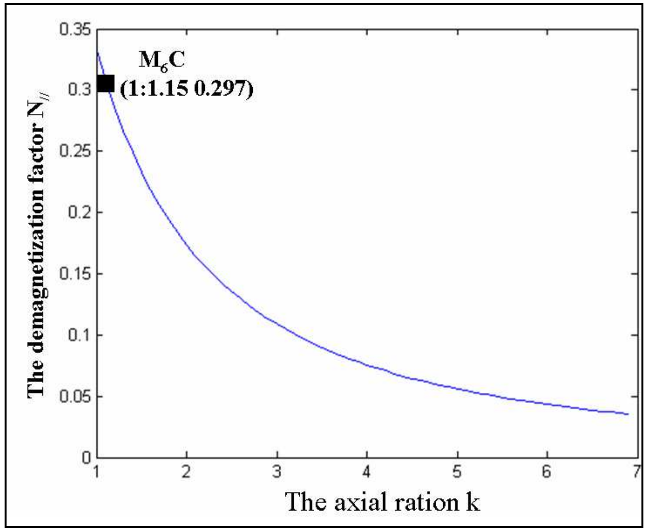


12 T

590°C for 3600 s



Identification of M_6C

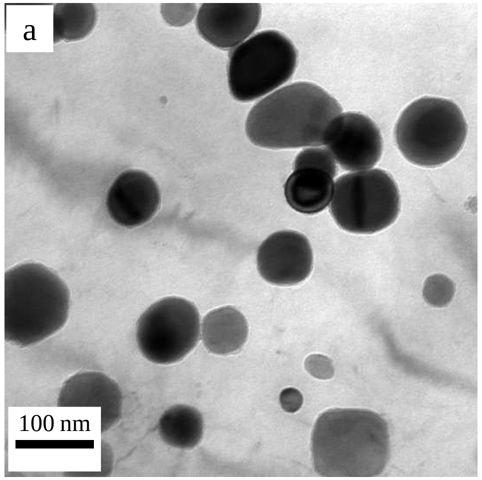


The demagnetization factor of M_6C

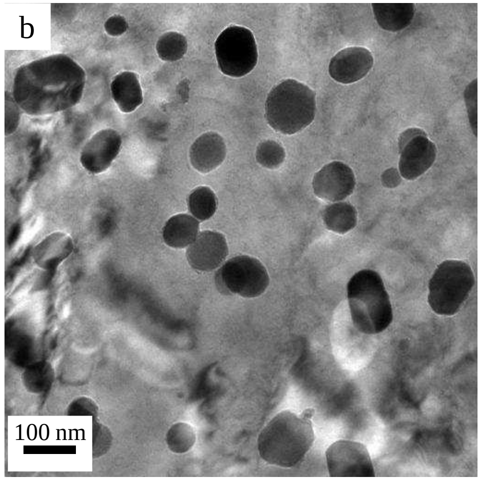
Morphology and EDS analysis at 530, 570, 610 ℃

	Without a 12 T magnetic field				With a 12 T magnetic field			
Time	20 s	60 s	600 s	3600 s	20 s	60 s	600 s	3600 s
Type	Fe_3C	Fe_3C M_2C M_3C	M_2C M_3C	M_6C	M_6C	M_6C	M_6C	M_6C
Carbide	Fe_3C	Fe_3C $(Fe, Mo)_2C$ $(Fe, Mo)_3C$	$(Fe, Mo)_2C$ $(Fe, Mo)_3C$	$(Fe, Mo)_6C$	$(Fe, Mo)_6C$	$(Fe, Mo)_6C$	$(Fe, Mo)_6C$	$(Fe, Mo)_6C$

Magnetic field promotes the M_6C precipitation



530-3600s-off



530-3600s-on

Magnetic field has no influence on the morphology of M_6C

Gibbs free energy

$$G^*(T,H) = G^*(T,0) - \int_0^M B \cdot dM$$

Chemical Gibbs free energy dependent on temperature

Magnetic Gibbs free energy mainly dependent on magnetic field and magnetization

Magnetic free energy

Carbides can be magnetized to some extent in a high magnetic field because Gibbs free energy is lowered in relation to their magnetization.

According to following equation, magnetic free energy change of carbide transformation can be expressed:

The corresponding energy (magnetic free energy ΔG^M) drop

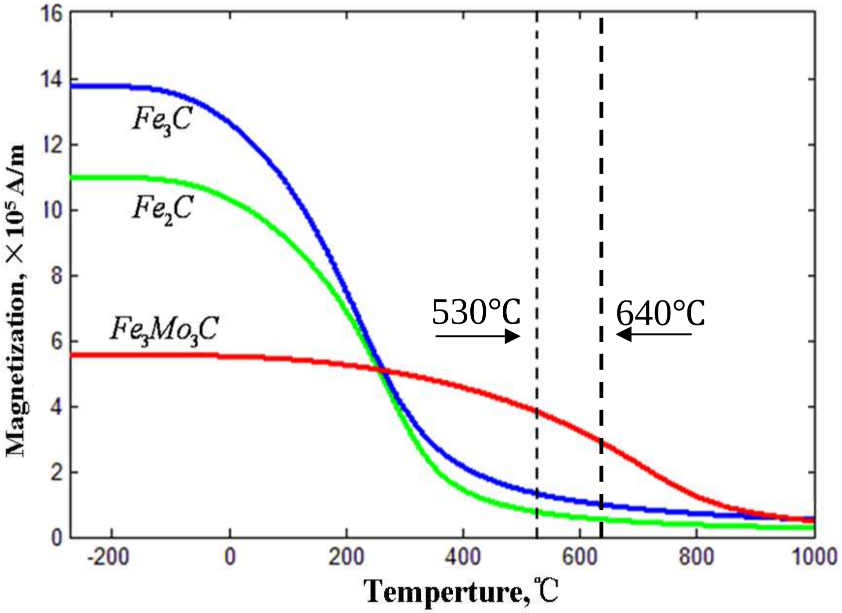
$$\Delta G^M = -\int_0^M \overrightarrow{B_0} \cdot d\overrightarrow{M}$$

$\overrightarrow{M}$ stands for the magnetization

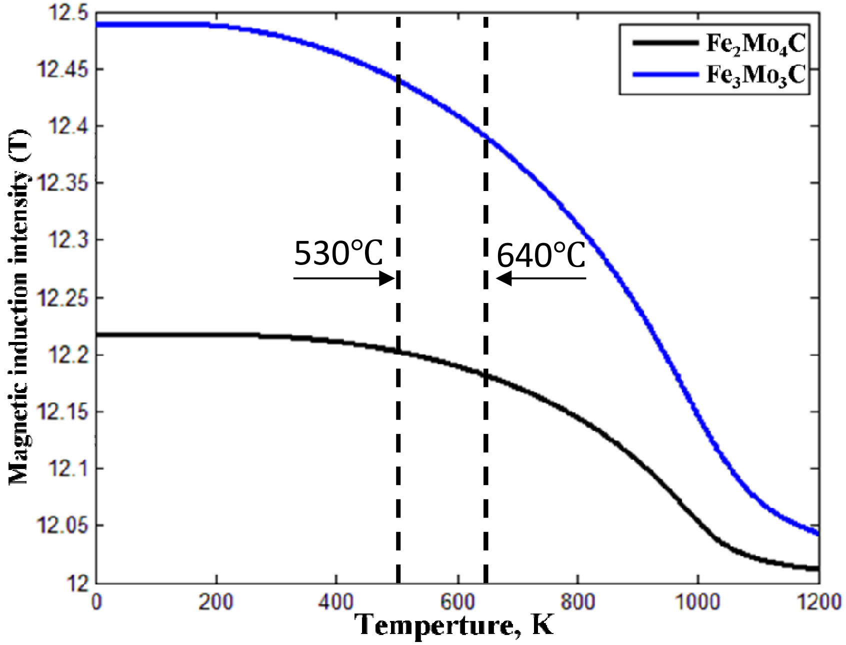
Induction of the applied magnetic field

$$\Delta G^M = -\int_0^M \overrightarrow{B} \cdot d\overrightarrow{M}$$

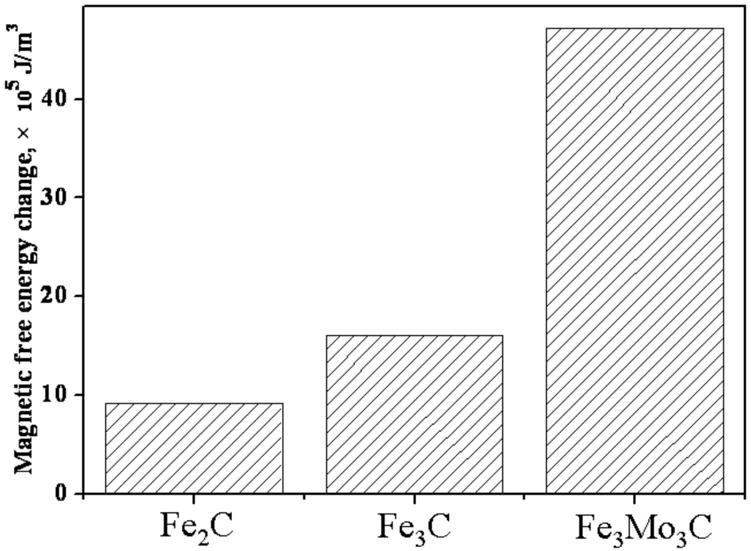
the internal field induction



The temperature variations of magnetization curve



The temperature variations of magnetic induction intensity of M_6C

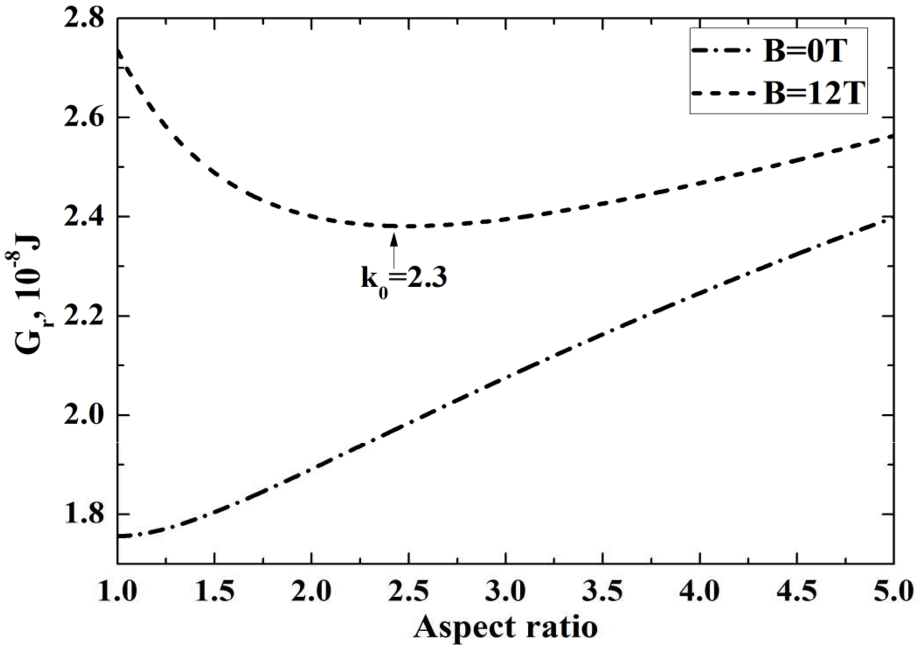


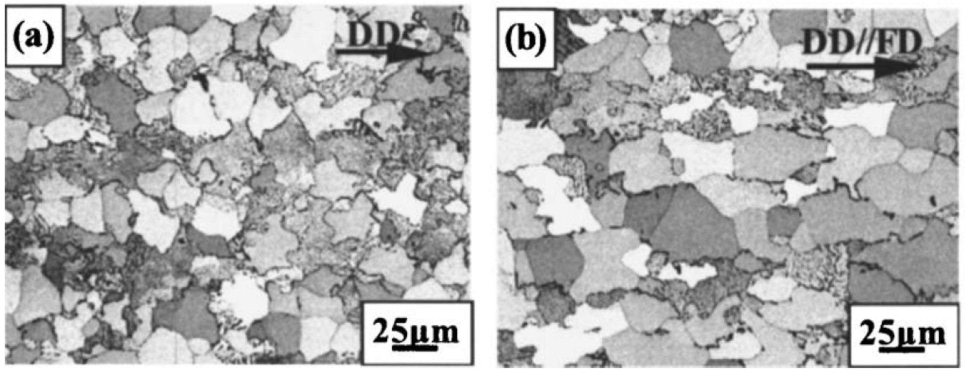
The magnetic free energy change of three carbides

$$\Delta G^{M} = -\int_{0}^{M} \overrightarrow{B} \cdot d\overrightarrow{M}$$

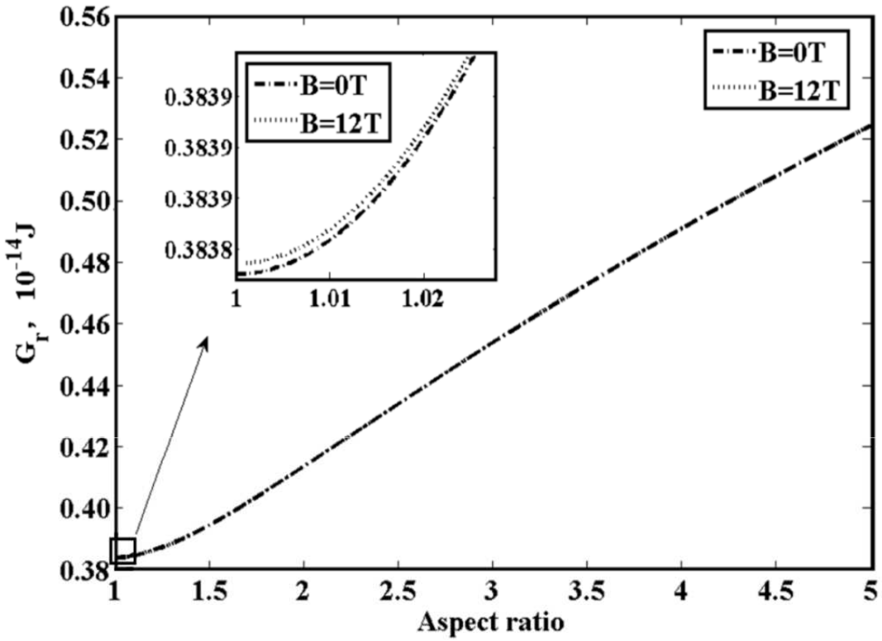
The effect of magnetic field on carbide particle morphology

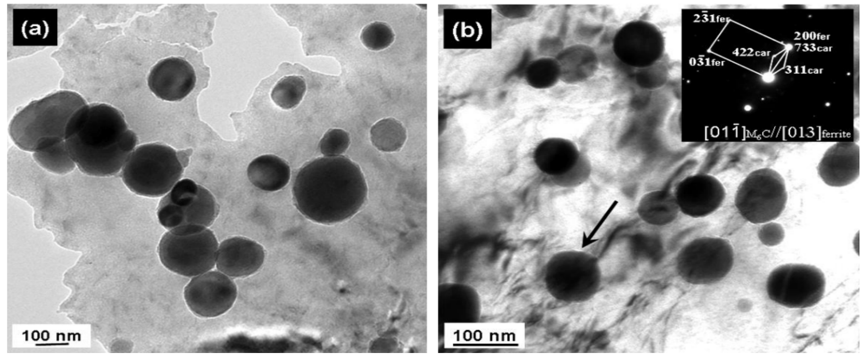
Ferrite





M_6C

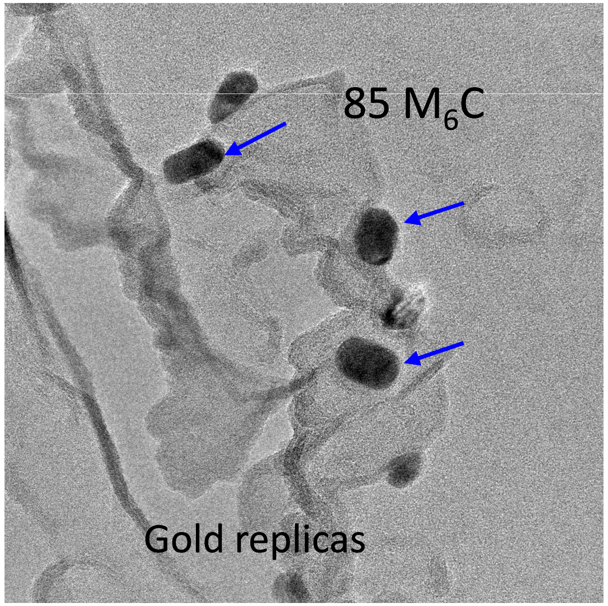




The variation curve of the relative free energy change with the aspect ratio

Measured concentration of substitutional solute atoms in the carbide of M_6C

Temp.	0 T				12 T			
	Fe (wt.%)		Mo (wt.%)		Fe (wt.%)		Mo (wt.%)	
	Average	Standard Deviation (σ)	Average	Standard Deviation (σ)	Average	Standard Deviation (σ)	Average	Standard Deviation (σ)
530°C	38.69	0.98	61.30	0.98	67.16	4.48	32.78	4.48



EDS analysis

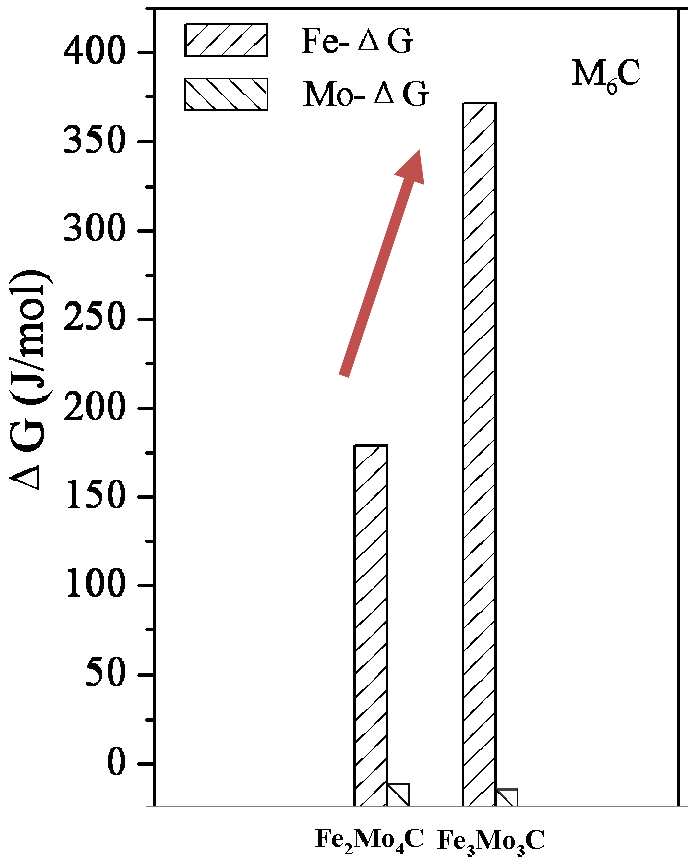
Higher than the composition without the magnetic field

0 T, Fe (wt.%)	
38-45 (700°C~900°C)	Ref. [Sato T, 1962]
36.4-38.6 (727°C)	Ref.[Uhrenius B,1975]
58.15 (874°C)	Ref. [Woodyatt LR,1979]

Measured concentration of substitutional solute atoms in the carbide of M_6C

Carbides	Metal	Magnetic moments(μ_B)
Fe_2Mo_4C Cubic a=11.26Å	Mo (48f)	-0.0273
	Mo (16d)	-0.0933
	Fe (32e)	1.331
	C (16c)	0.00047
Fe_3Mo_3C Cubic a=11.11Å	Fe (32e)	1.864
	Fe (16d)	1.815
	Mo (48f)	-0.0728
	C (16c)	0.0108

First principle calculation results



The magnetic free energy change of Fe and Mo atoms in different carbides M_6C (Fe_2Mo_4C, Fe_3Mo_3C).

Conclusion

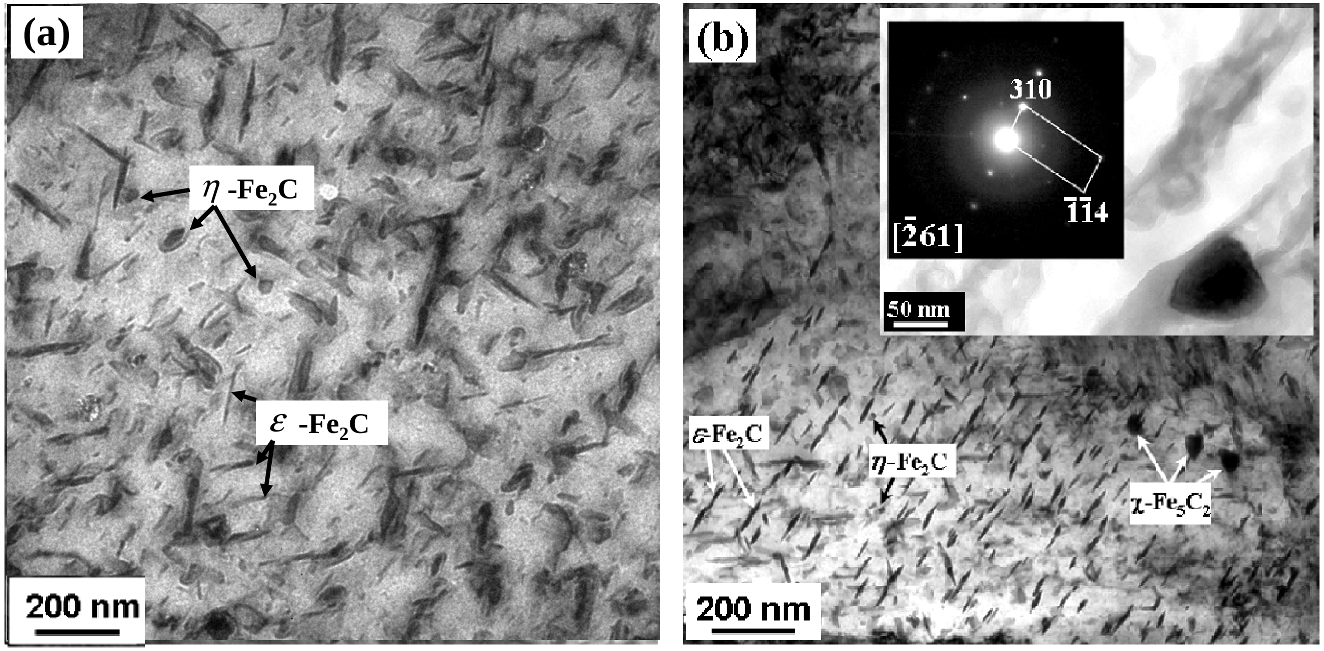
The concentration of substitutional solute atoms Fe and Mo in the carbide of $(Fe,Mo)_6C$ was influenced by high magnetic field. The change of concentration of substitutional solute atoms Fe and Mo was caused by their differences in magnetic moments.

Part Ⅱ

The influence of the high magnetic field on the alloy carbide in tempering transformation of Fe-C-Mo alloy

Magnetic field promotes the precipitation of Fe_5C_2

0 T



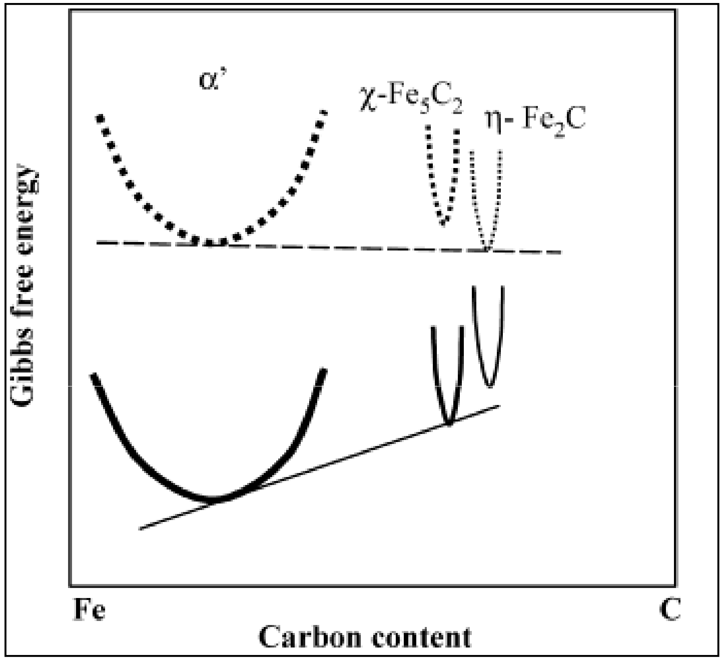
12 T

Tempered at 200°C for 3600 s

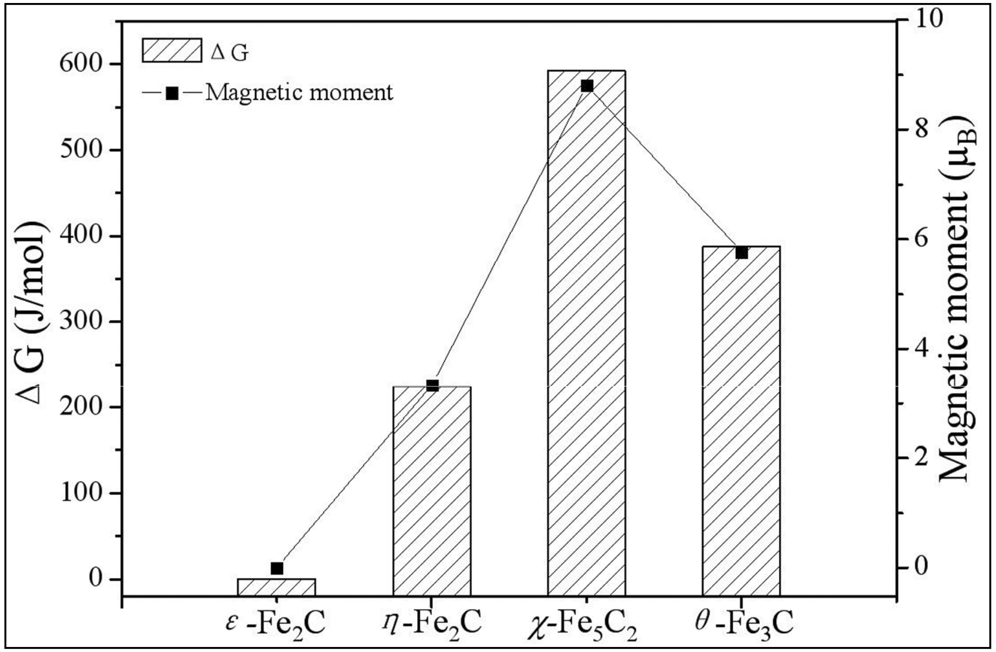
In conclusion

Tempering time	600 s (B=0T)	600 s (B=12 T)	3600 s (B=0T)	3600 s (B=12 T)
Carbide type	ε-Fe_2C η-Fe_2C	ε-Fe_2C η-Fe_2C	ε-Fe_2C η-Fe_2C	ε-Fe_2C η-Fe_2C χ-Fe_5C_2

The magnetic Gibbs free energy change



Y D Zhang et al. ISIJ International (2005)



The magnetic free energy change and the magnetic moments of the metastable carbides

Conclusion II

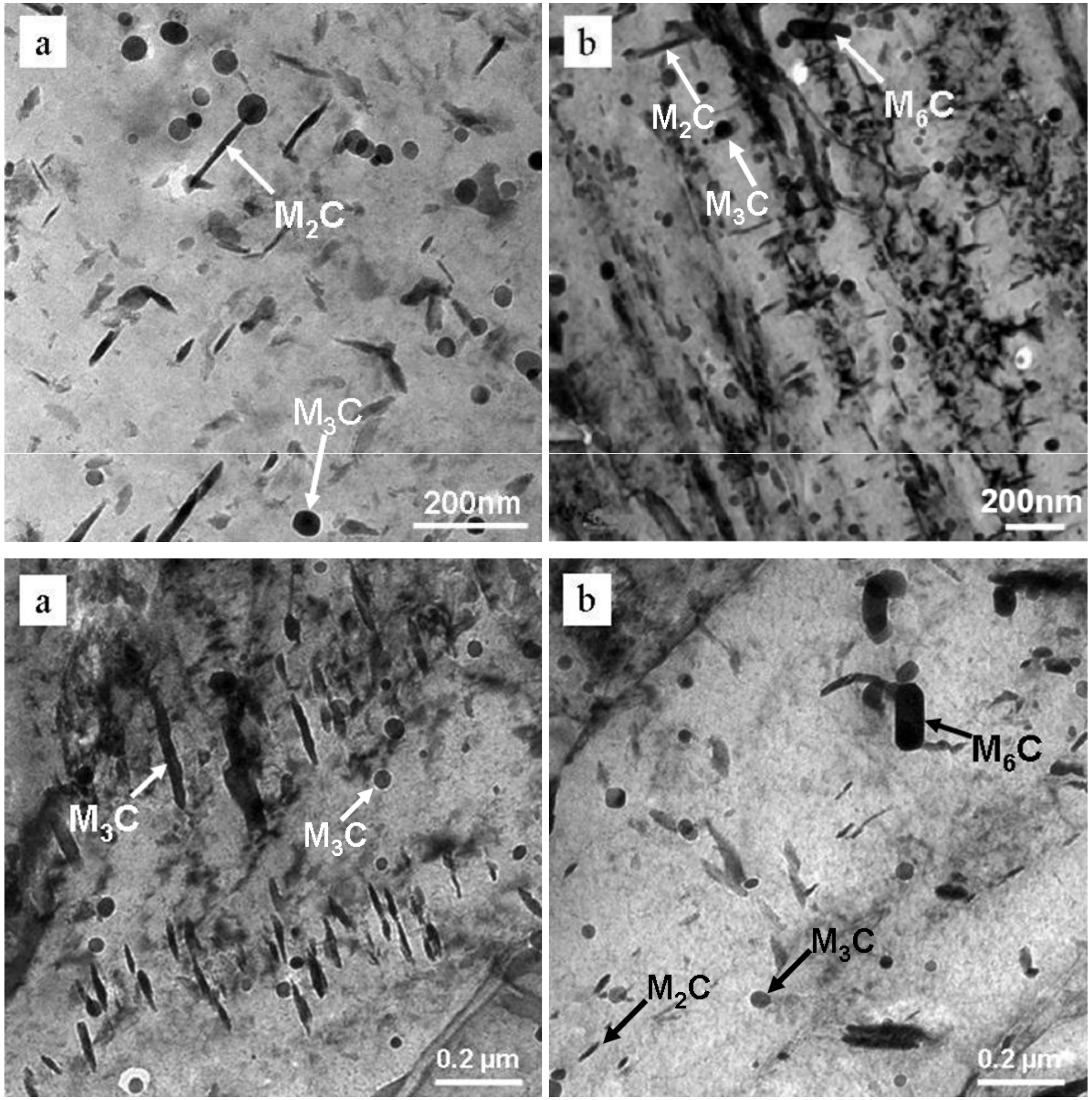
Among the metastable phasesε-Fe_2C, η-Fe_2C, χ-Fe_5C_2, and the stable phase θ-Fe_3C, χ-Fe_5C_2 has the highest moment, resulted in the stability under high magnetic field through magnetization. Therefore, the influence of the magnetic field on the Gibbs free energy of χ-Fe_5C_2 is the most remarkable.

The effect of the magnetic field on the carbide at 530°C

600 s

3600 s

0 T

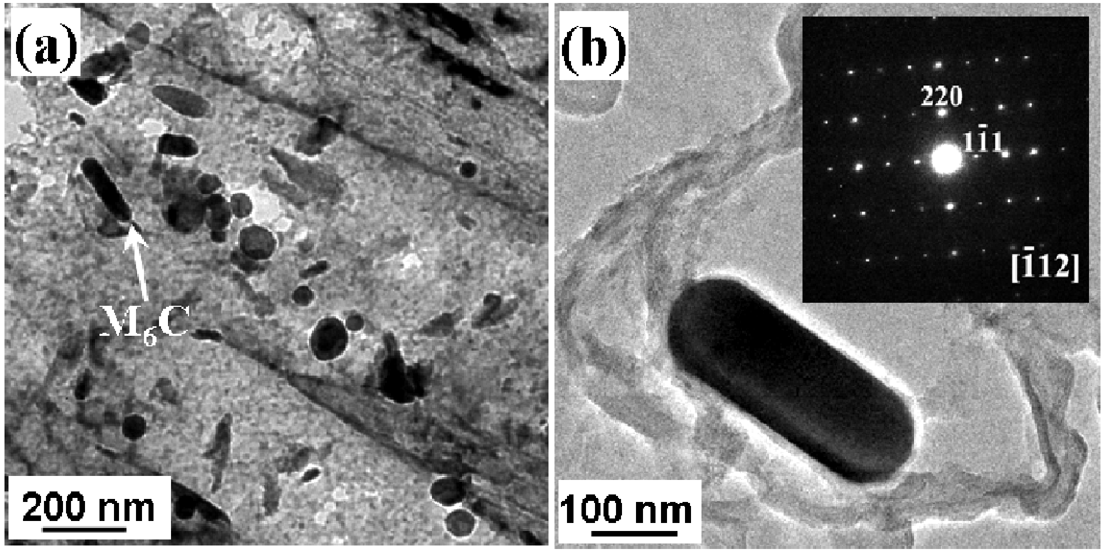


600 s M_6C

3600 s M_6C

12 T

The identification of M_6C carbide

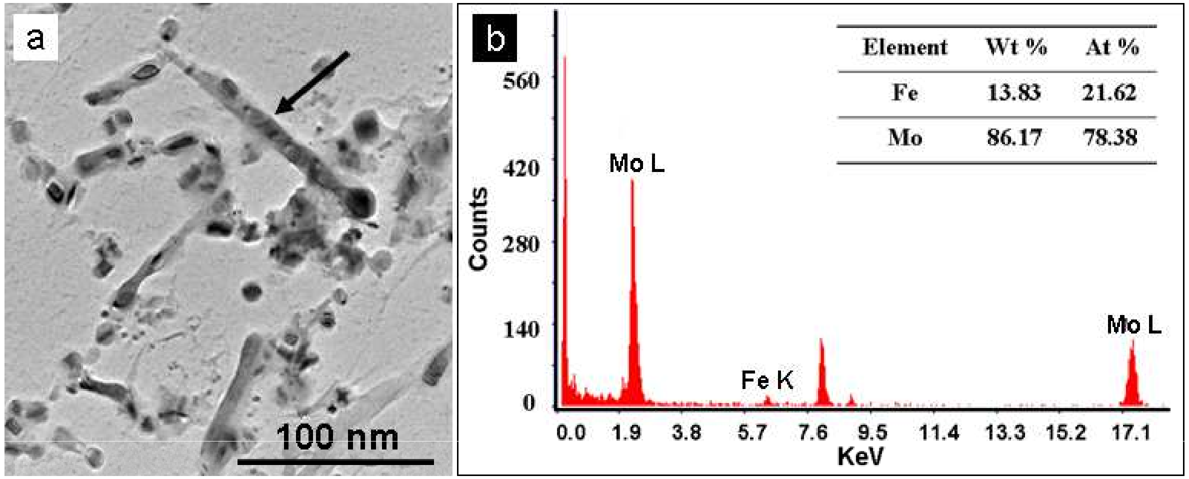


The magnetic field promotes the precipitation of M_6C

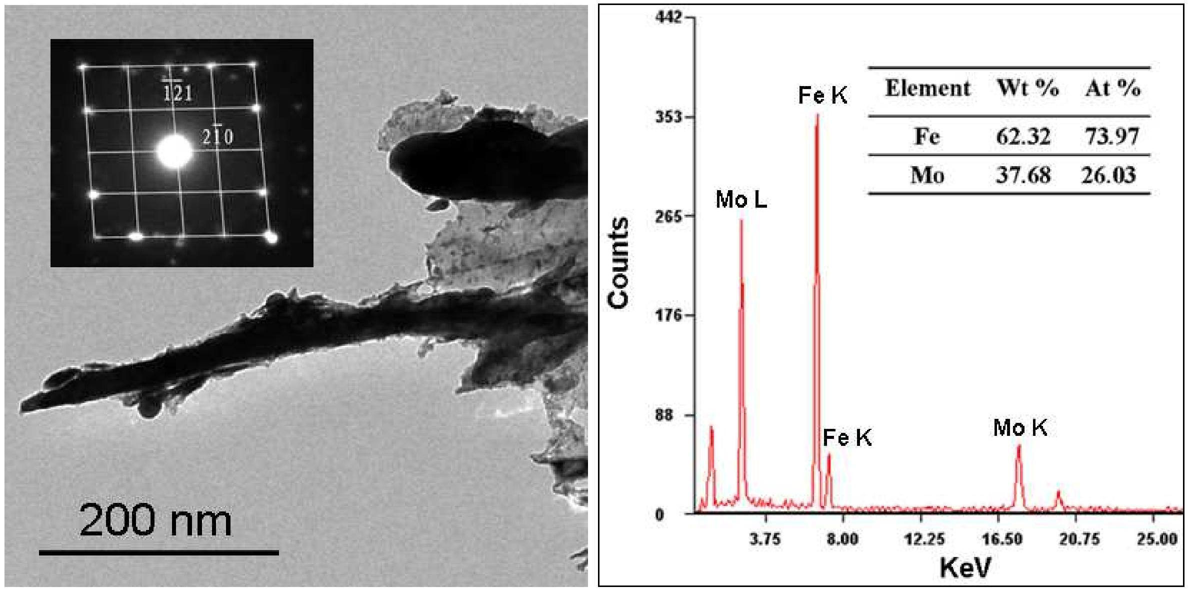
Conclusion

	Without magnetic field		With a 12-T magnetic field	
Time	600 s	3600 s	600 s	3600 s
Type	M_2C, M_3C	M_2C, M_3C	M_2C, M_3C, M_6C	M_2C, M_3C, M_6C

Measured concentration of substitutional solute atoms in the carbide of M_2C and M_3C

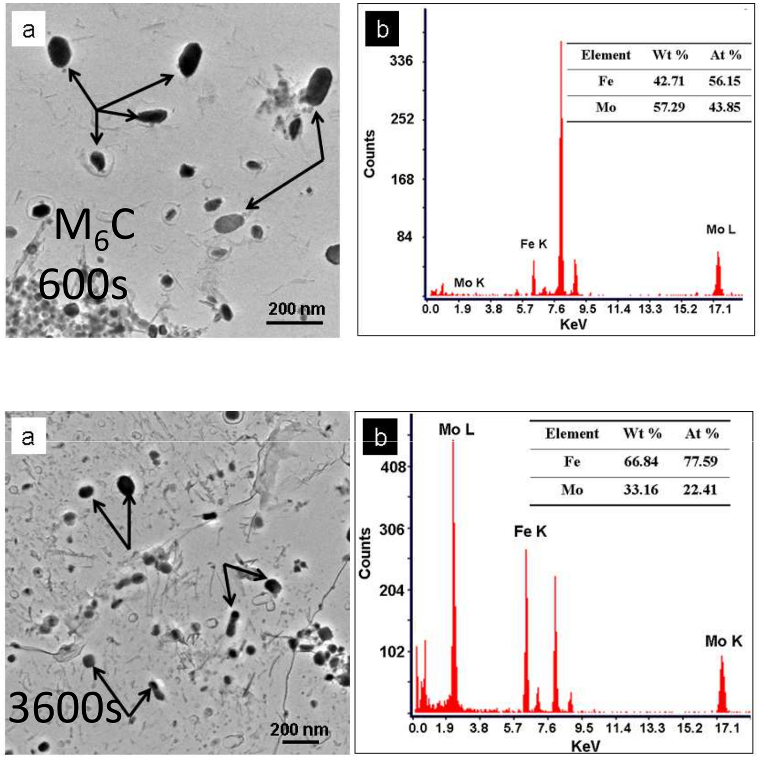


M_2C

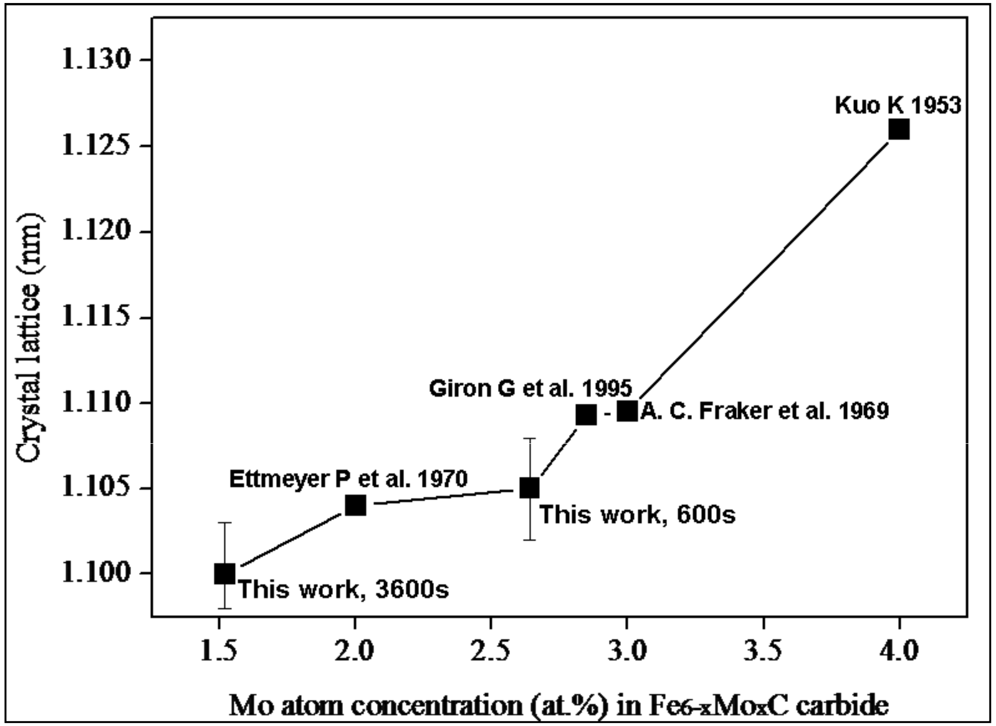


M_3C

Measured concentration of substitutional solute atoms in the carbide of M_6C

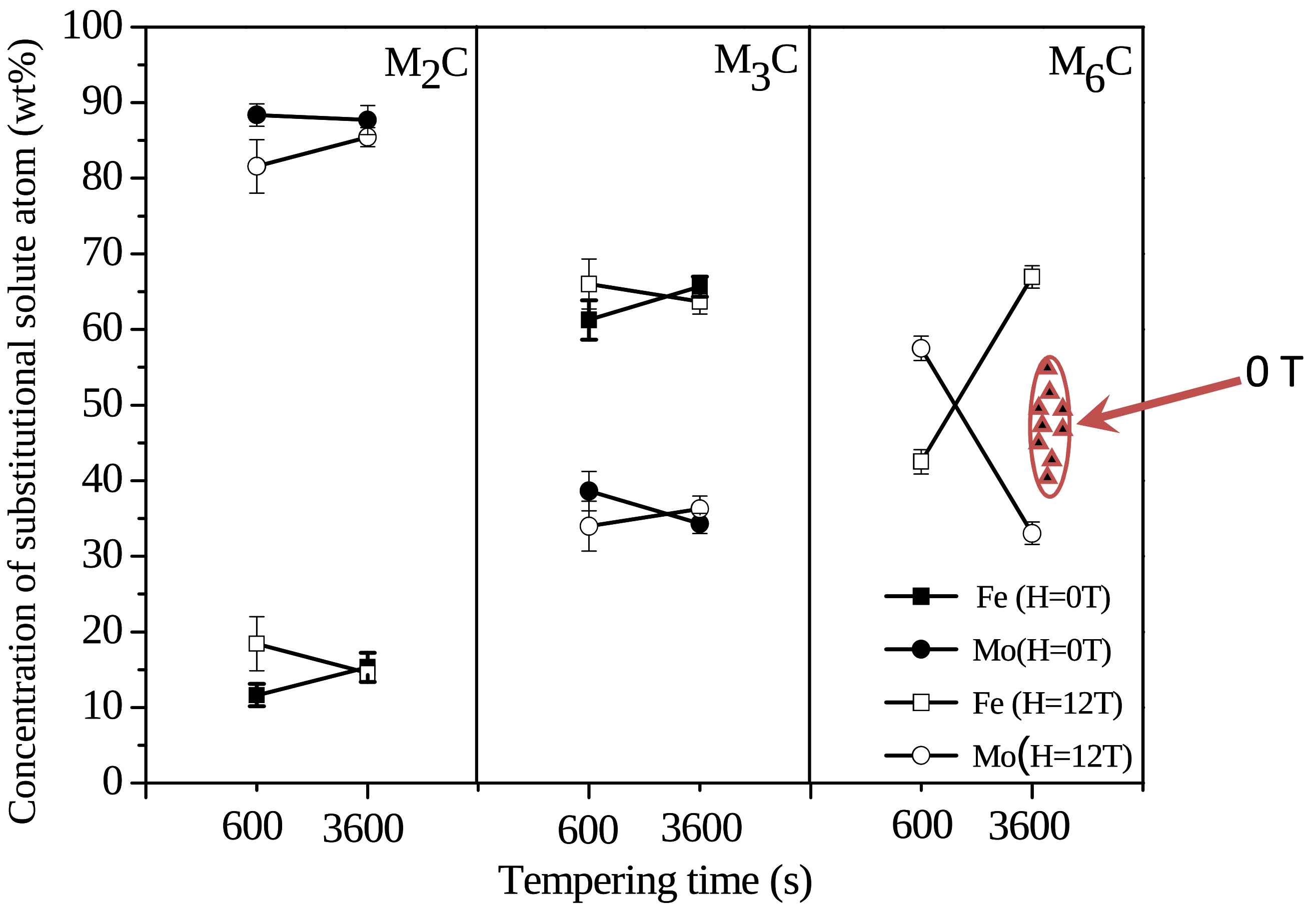


Carbon extraction replicas specimen and the average EDS analysis of $(Fe, Mo)_6C$



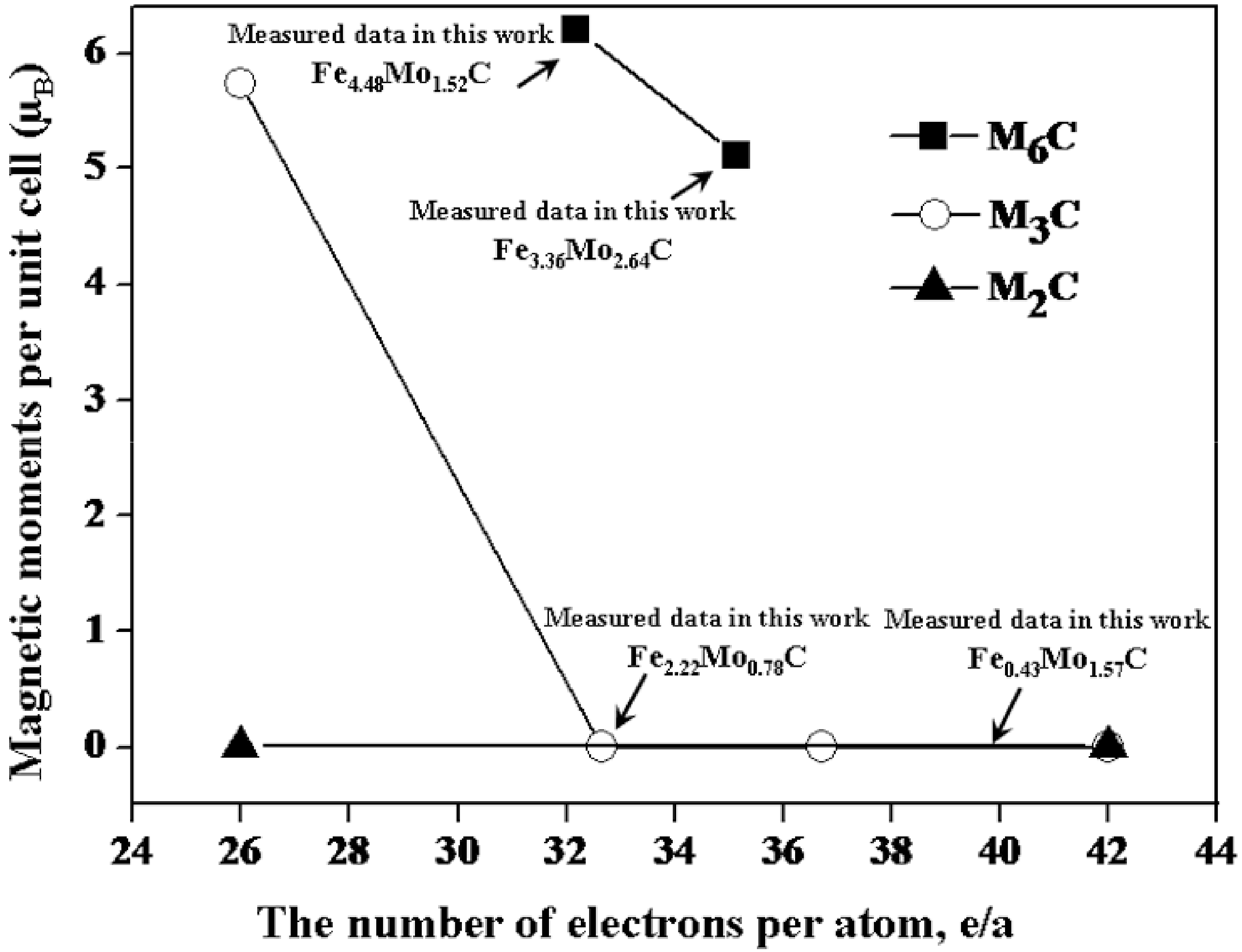
Lattice constants of Fe6-xMoxC (where x is the atomic concentration of Mo).

Measured concentration of substitutional solute atoms in the carbide of M_6C



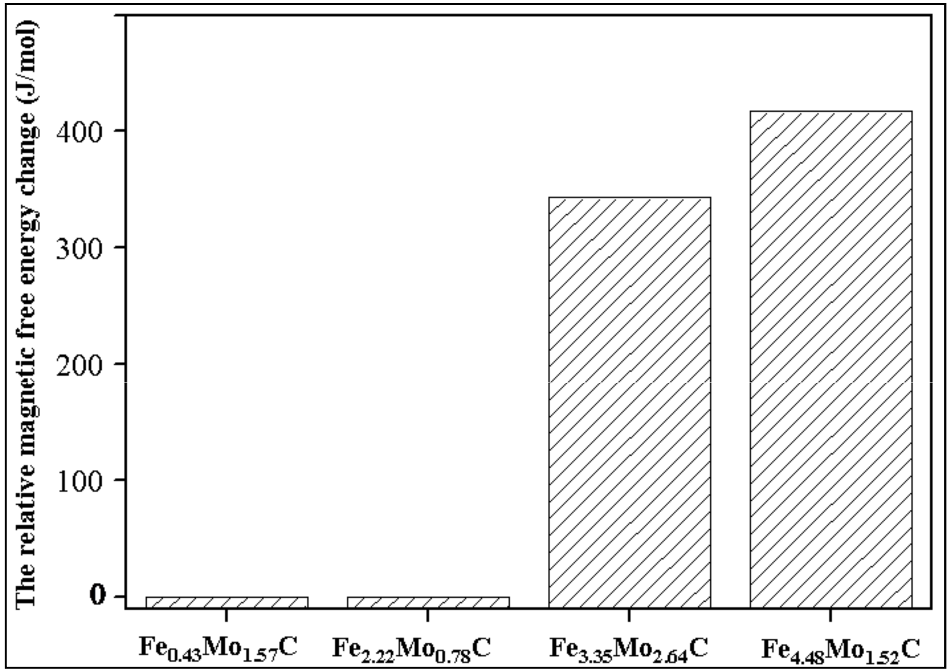
Regarding to the carbides of M_2C and M_3C, no obvious concentration change was detected when 12-T magnetic field was applied. However, regarding the carbide of M_6C, the concentration of Fe atom was increased, whereas the concentration of Mo atom was decreased when a 12-T magnetic was applied.

The calculated Fe magnetic moment of carbides

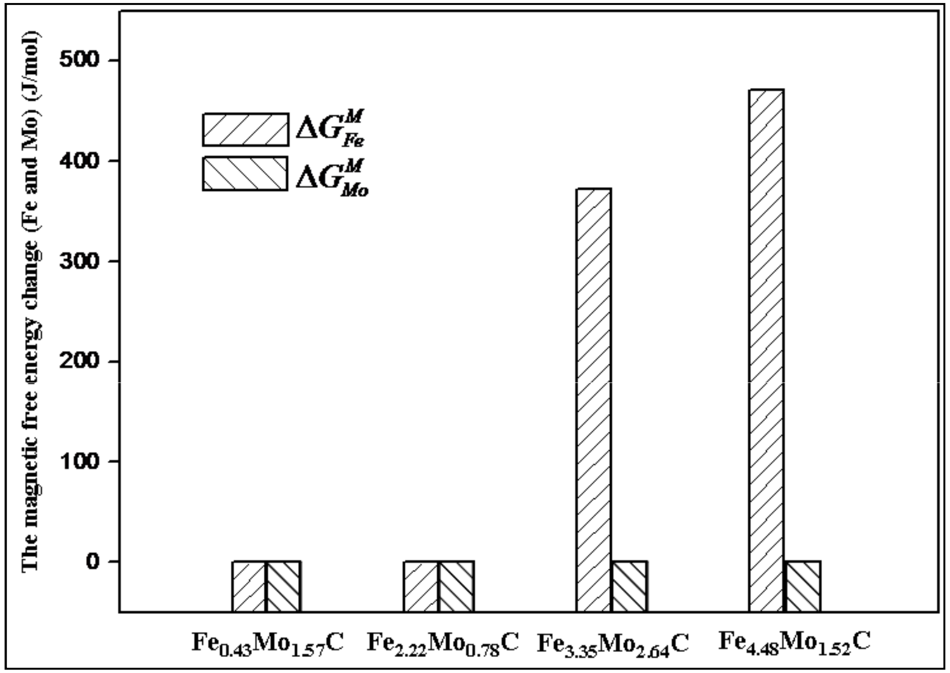


The calculated magnetic moments per unit cell from the first principle calculation in M_6C, M_3C and M_2C carbides as a function of the number of electrons per atom. The two arrows represent the experimentally measured data.

The magnetic Gibbs free energy change

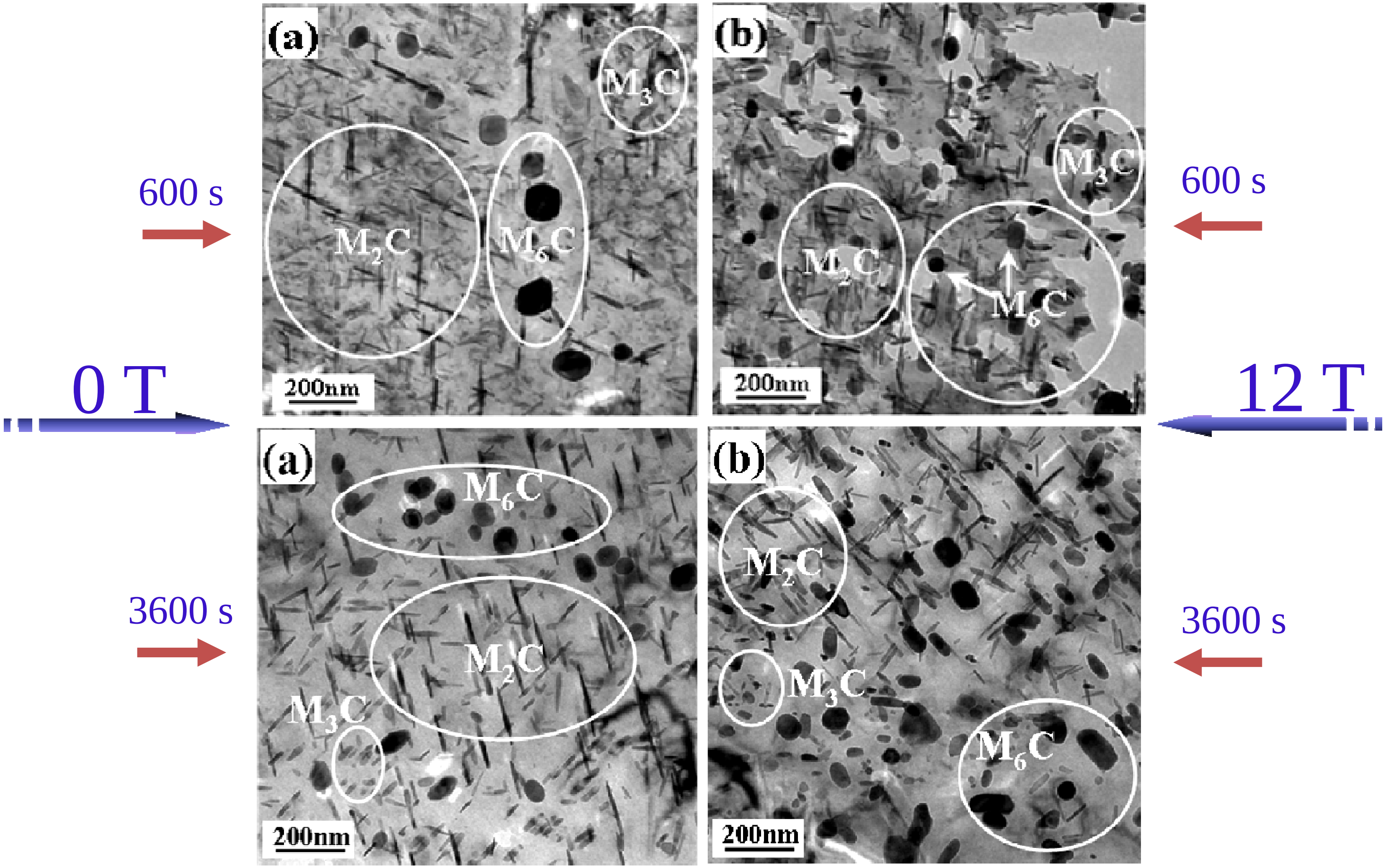


The relative magnetic free energy change for M_2C ($Fe_{0.43}Mo_{1.57}C$), M_3C ($Fe_{2.22}Mo_{0.78}C$), M_6C ($Fe_{3.36}Mo_{2.64}C$ and $Fe_{4.48}Mo_{1.52}C$), respectively.



The magnetic free energy change of Fe and Mo atoms

The effect of the magnetic field on alloy carbide at 700°C



Morphology of alloy carbide tempered at 700 °C

The effect of the magnetic field on the carbide at 700°C

No influence

600 s (0 T and 12 T)	3600 s (0 T and 12 T)
M_2C, M_3C, M_6C	M_2C, M_3C, M_6C

Reason

$$\chi = \frac{M}{H}$$

$$H = \frac{B}{\mu_0} - M$$

Carbides	Fe_2C	Fe_3C	Fe_3Mo_3C
Magnetic susceptibility	0.0048	0.0063	0.0199

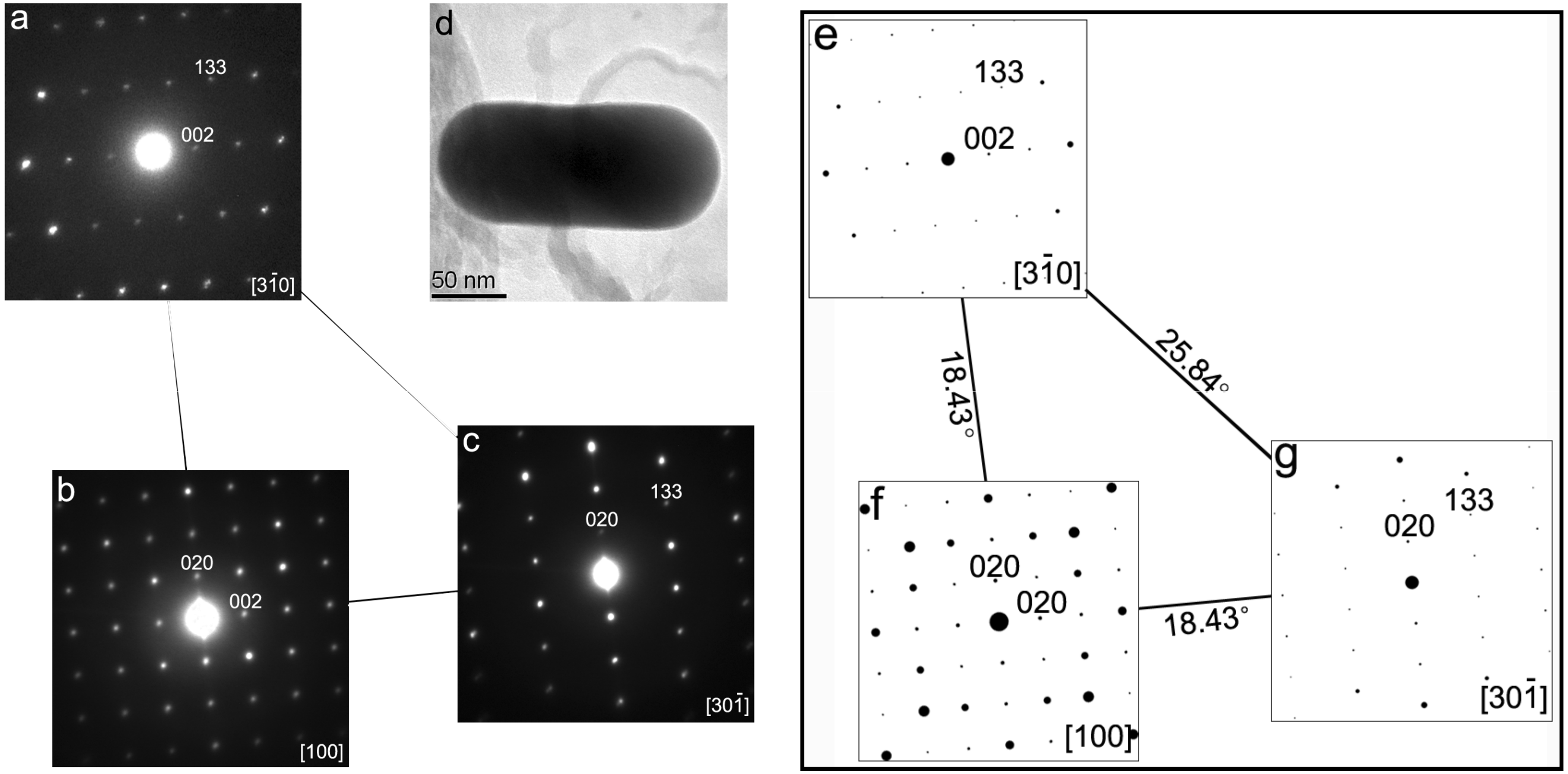
Conclusion

There was no pronounced effect of high magnetic field on the precipitation sequence of alloy carbides when specimens were tempered at 700° C. Because they were changed into paramagnetic phases at higher temperature.

Part III

The influence of the high magnetic field on the alloy carbide in tempering transformation of 2.25Cr-Mo alloy

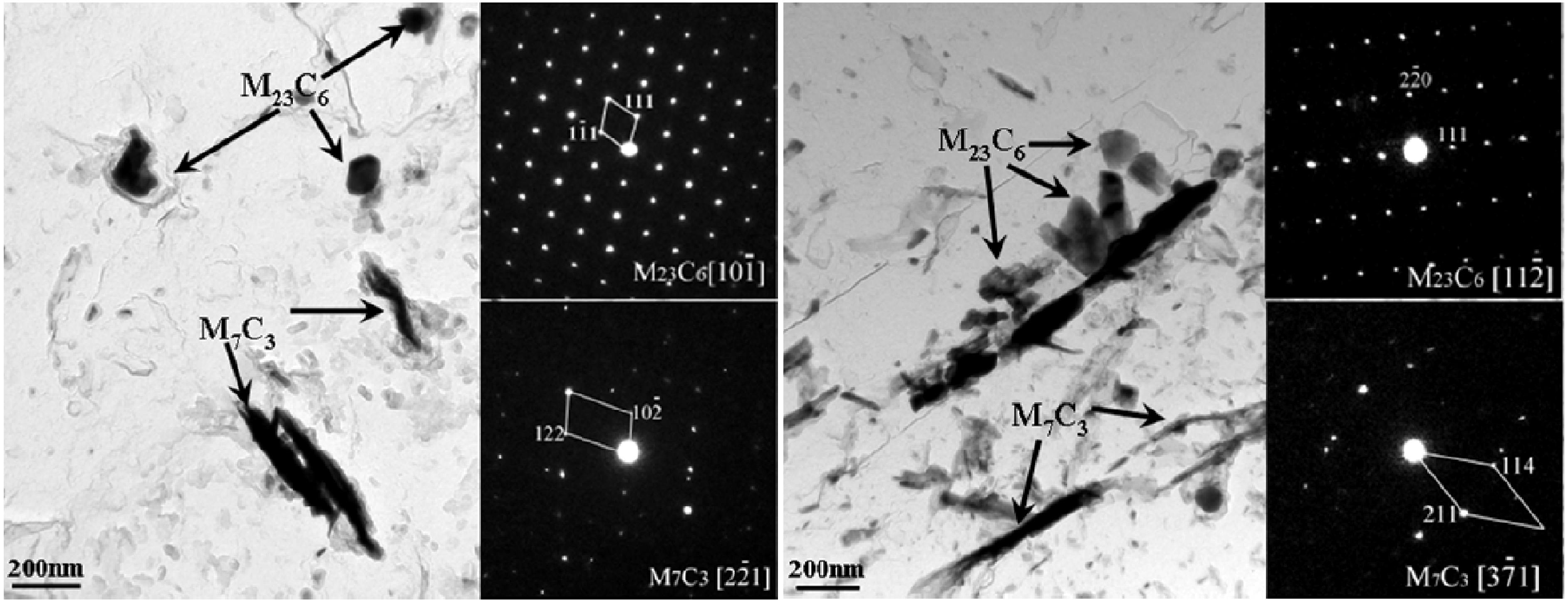
The identification of $M_{23}C_6$ carbide



The morphology of $M_{23}C_6$ carbide and the selected area electron diffraction

The effect of the magnetic field on the carbide at 550°C

12 Tesla



600 s, 12 T

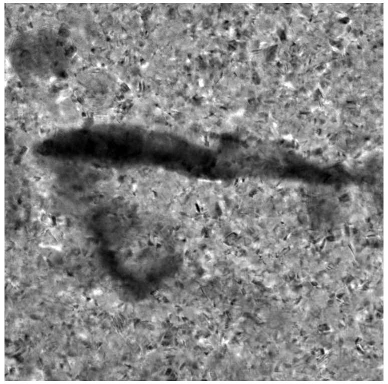
3600 s, 12 T

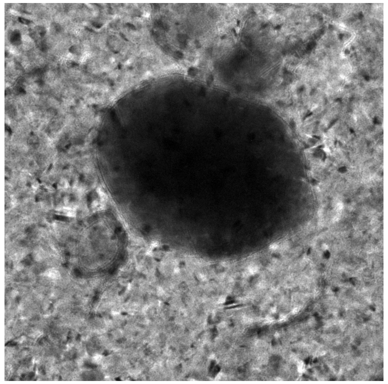
The precipitation sequence

Without a magnetic field			With a 12-T magnetic field	
Time	600 s	3600 s	600 s	3600 s
Type	M_2C, M_3C	M_2C, M_3C	M_2C, M_3C M_7C_3, $M_{23}C_6$	M_2C, M_3C M_7C_3, $M_{23}C_6$
Carbides	$(Fe, Cr, Mo)_2C$ $(Fe, Cr, Mo)_3C$	$(Fe, Cr, Mo)_2C$ $(Fe, Cr, Mo)_3C$	$(Fe, Cr, Mo)_2C$ $(Fe, Cr, Mo)_3C$ $(Fe, Cr, Mo)_7C_3$ $(Fe, Cr, Mo)_{23}C_6$	$(Fe, Cr, Mo)_2C$ $(Fe, Cr, Mo)_3C$ $(Fe, Cr, Mo)_7C_3$ $(Fe, Cr, Mo)_{23}C_6$

$M_{23}C_6$ and M_7C_3 particles

Gold replicas





M_7C_3 6:1

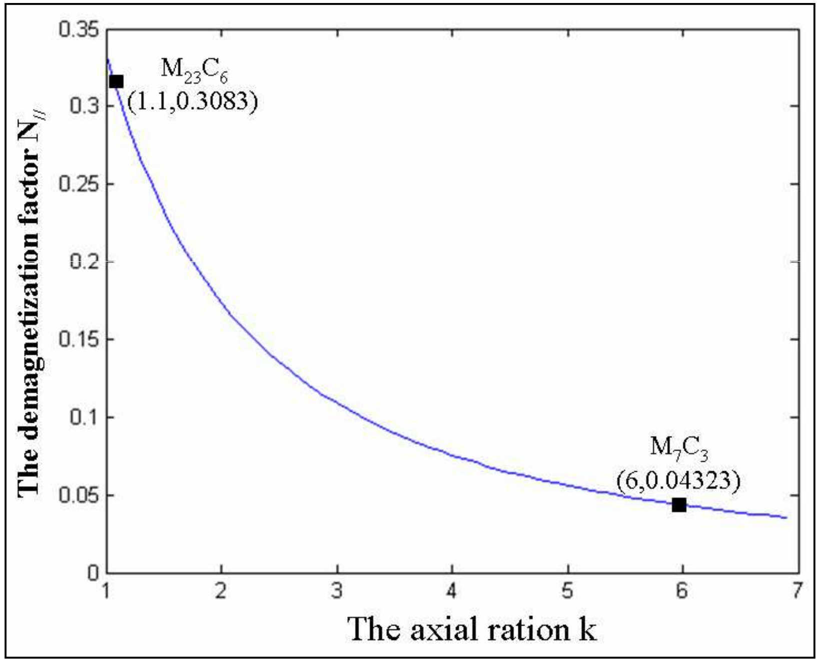
$(Cr_{4.02}Fe_{18.98})C_6$

$M_{23}C_6$ 1:1

$(Cr_{2.24}Fe_{4.76})C_3$

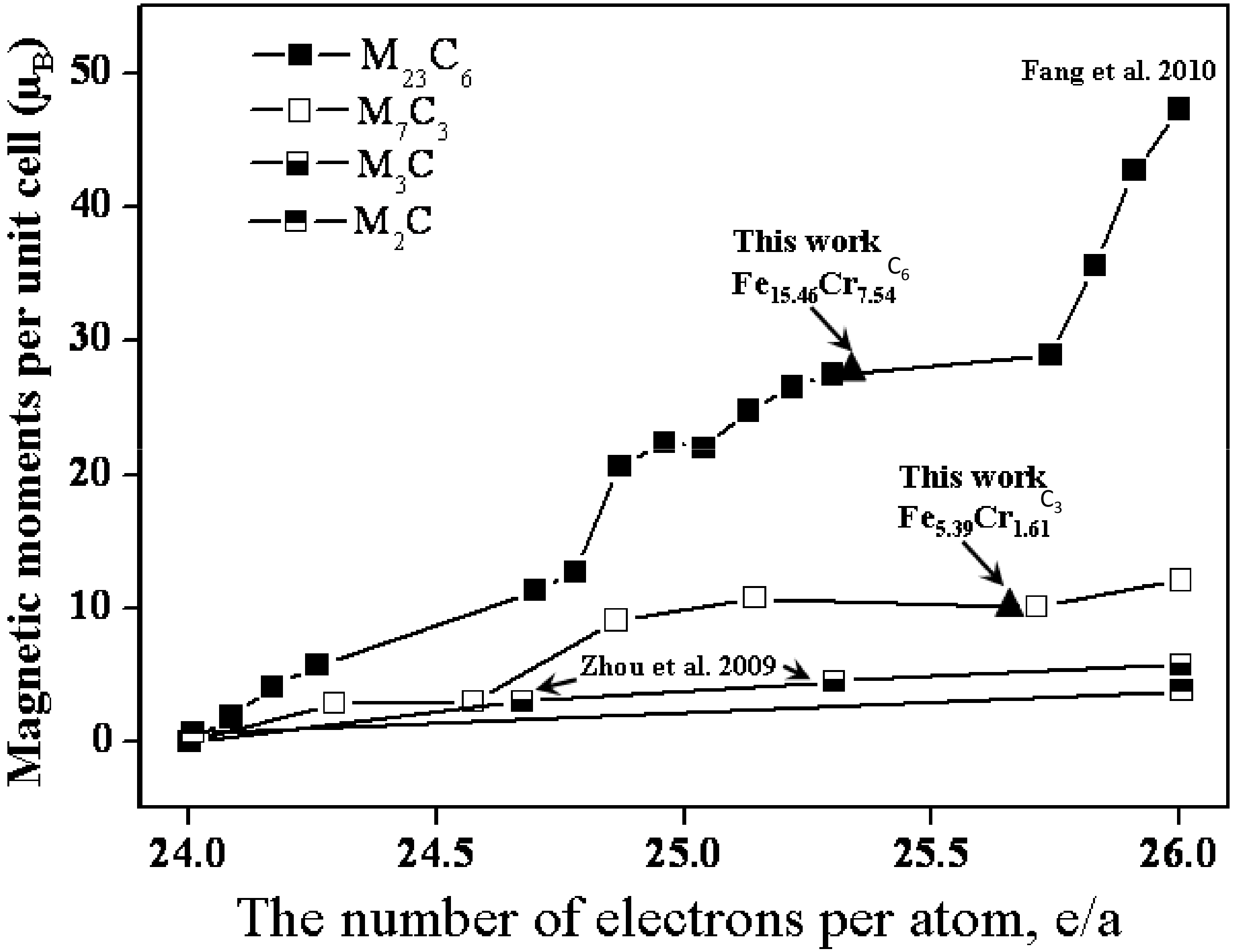
$M_{23}C_6$	Fe	Cr	Mo	Mn
Thermo-Cal	25.2	49.8	19.5	0.03
J-MatPro	25.1	48.3	19.4	0.25
Experimental	70.35	14.16	9.30	6.19

$$N_{//} = \frac{4\pi}{k^2-1}\left[\frac{k}{\sqrt{k^2-1}}\ln(k+\sqrt{k^2-1})-1\right]$$

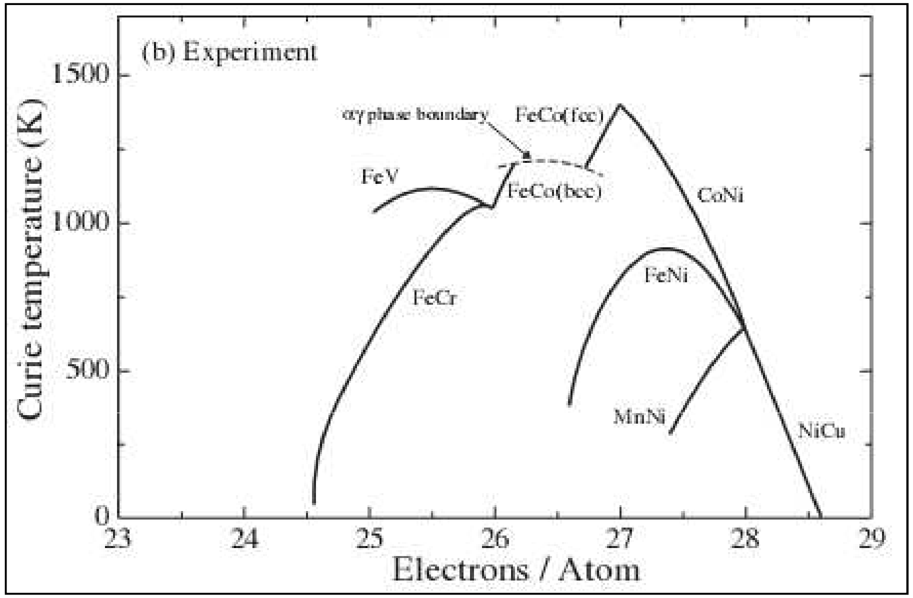


The demagnetization factor

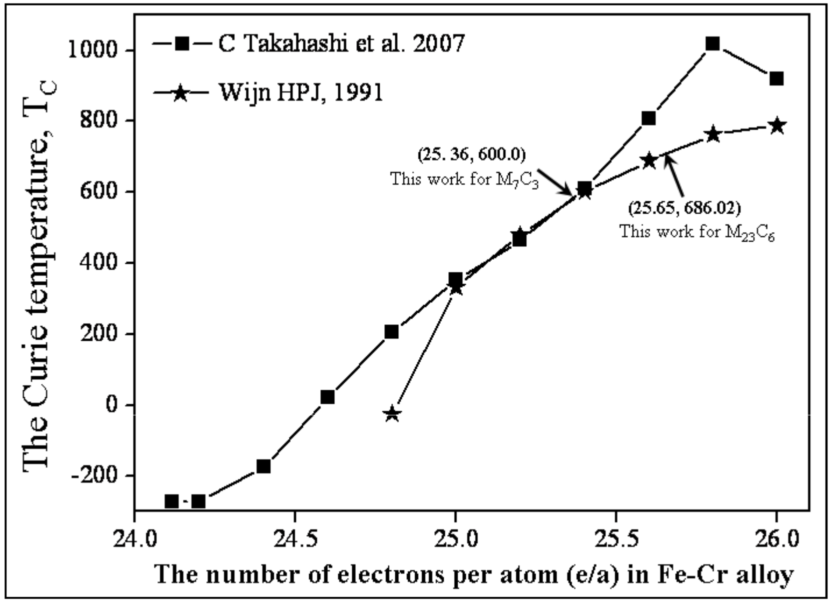
First principle calculation



Curie temperature



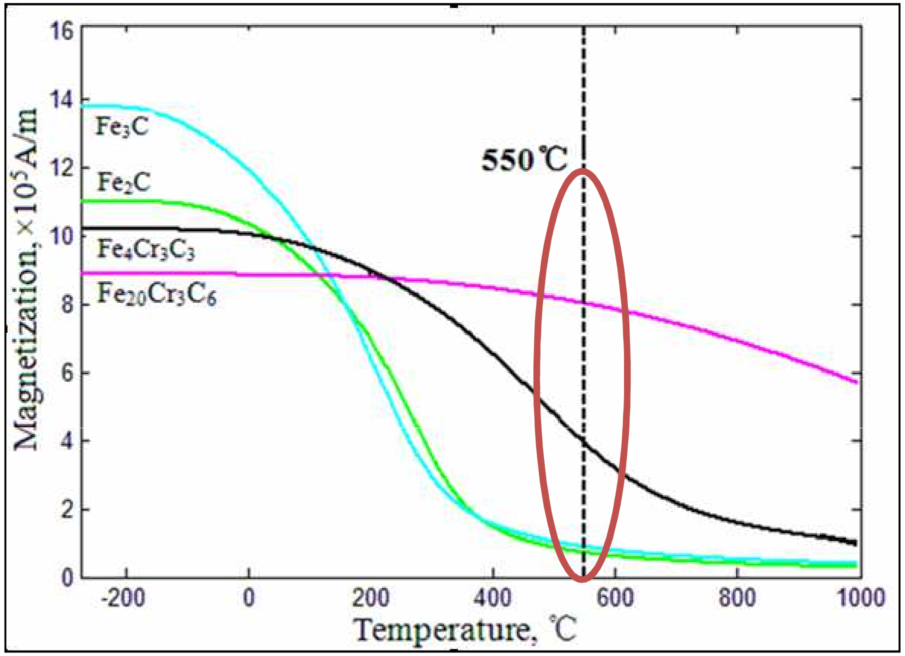
Wijn H P J 1991 *Magnetic Properties of Metals*



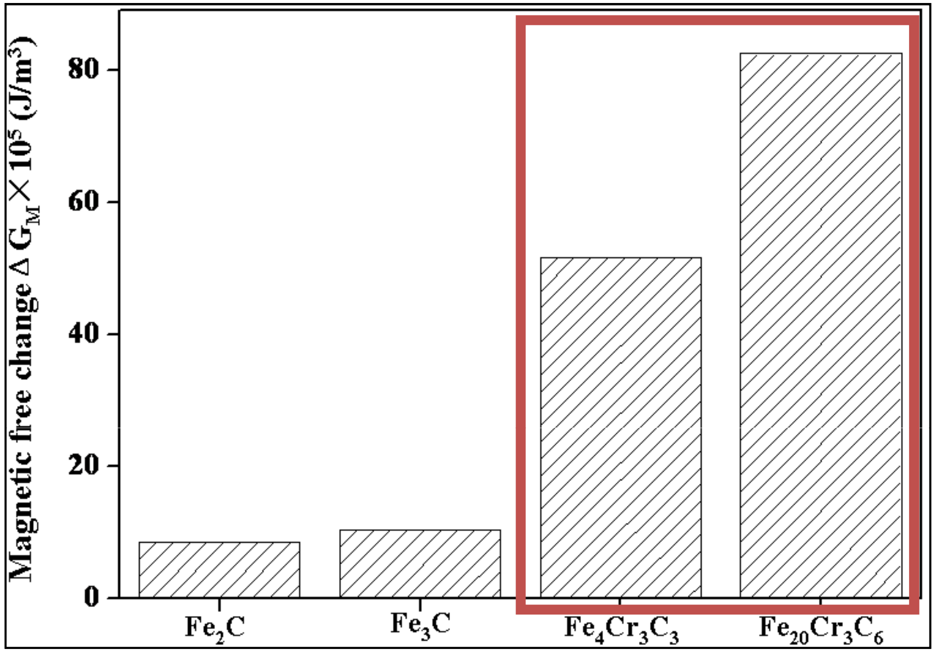
The Curie temperature in experiment of Fe-Cr alloy

The Curie temperature in theory of Fe-Cr alloy

M-T and magnetic Gibbs free energy



The magnetization curve with the temperature



The magnetic free energy change

Magnetic field promotes the precipitation $M_{23}C_6$ and M_7C_3 → **Conclusion**

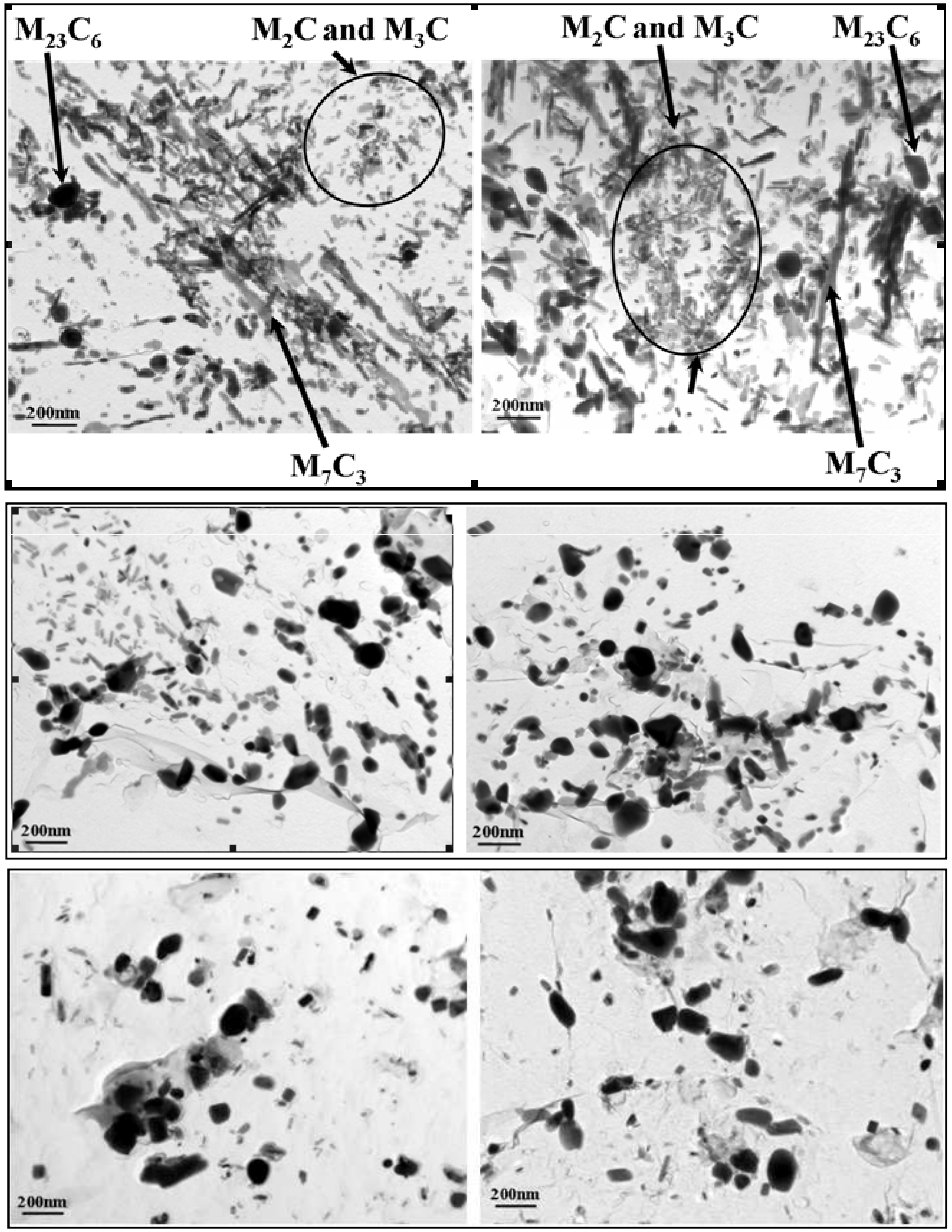
The effect of the magnetic field on the carbide at 700°C

0 T

600 s

3600 s

21600 s



12 T

600 s

3600 s

21600 s

The effect of the magnetic field on the carbide at 700℃

No influence

	0 T	12 T
Type	M_2C, M_3C M_7C_3, $M_{23}C_6$	M_2C, M_3C M_7C_3, $M_{23}C_6$

Reason

$$\chi = \frac{M}{H}$$

$$H = \frac{B}{\mu_0} - M$$

Carbides	Fe_2C	Fe_3C	$Fe_4Cr_3C_3$	$Fe_{20}Cr_3C$
Magnetic susceptibility	0.0048	0.0063	0.0216	0.0481

Conclusion

There was no pronounced effect of high magnetic field on the precipitation sequence of alloy carbides when specimens were tempered at 700° C. Because they were changed into paramagnetic phases at higher temperature.

Conclusions

◆ The magnetic Gibbs free energy change determined the precipitation behaviors of the M_6C, $M_{23}C_6$ and M_7C_3. In essence, the higher Fe atom content in carbides M_6C, $M_{23}C_6$ and M_7C_3 carbide makes the magnetic moment increased remarkably, which thus reduces the magnetic Gibbs free energy of alloy carbides.

◆ There was no pronounced influence on the precipitation behaviors of paramagnetic alloy carbides when specimens were tempered at high temperature (700°C).

Challenges

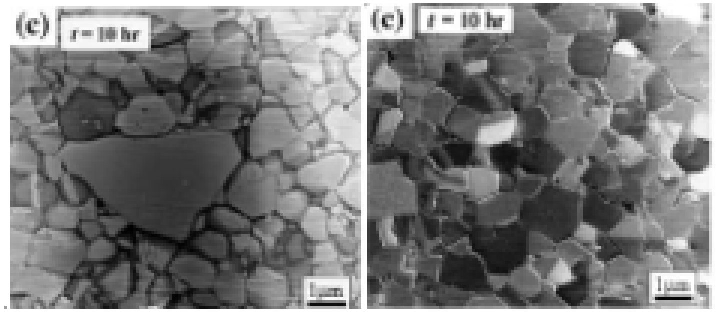
- Further detailed descriptions of the influence of the magnetic field on the phase transformation.

- The systematic research on the multi-action considering to the temperature and magnetic field.

Thank you

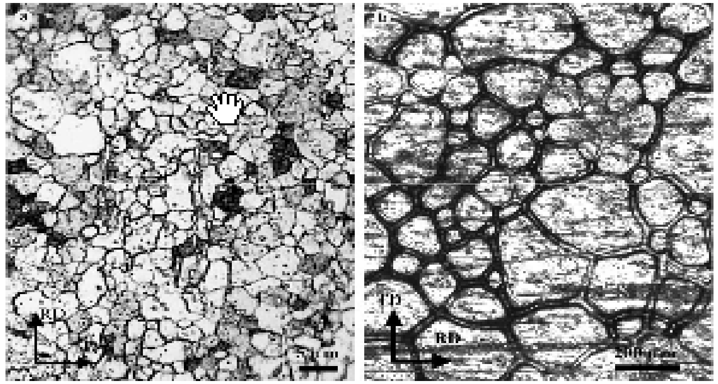
Background

Magnetic field increase the nucleation rate, facilitating more uniform grain distribution



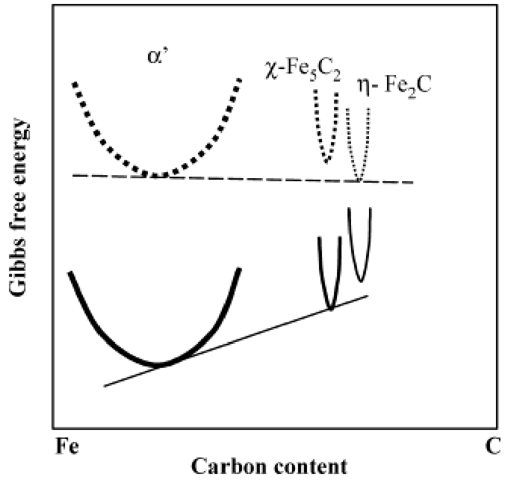
Watanabe T, 2006

Magnetic field changes the morphology

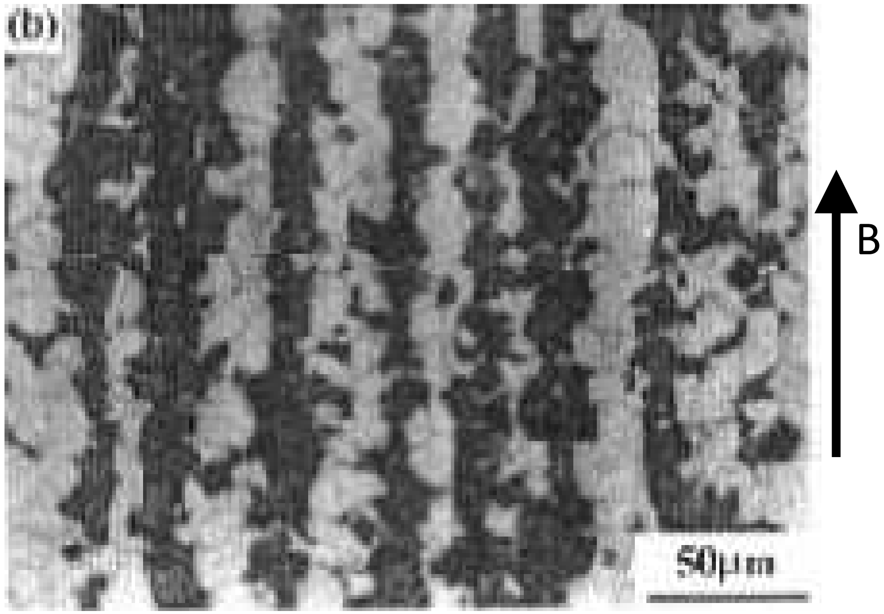


Sheikh-Ali AD, 2002

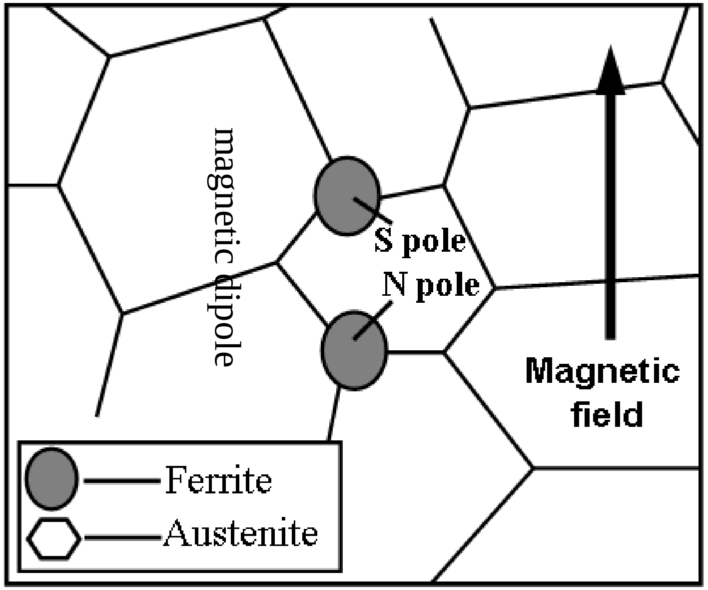
Magnetic field changes the Gibbs free energy resulted in phase transformation



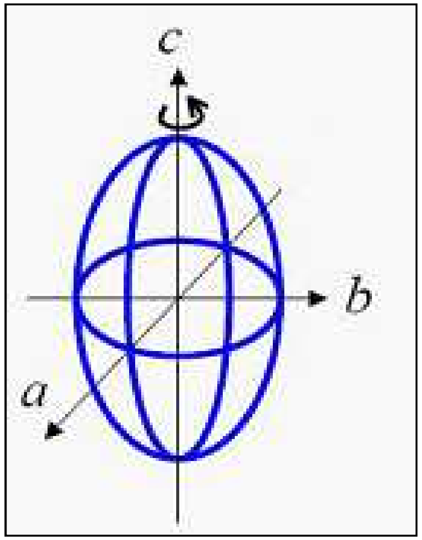
YD Zhang, 2004



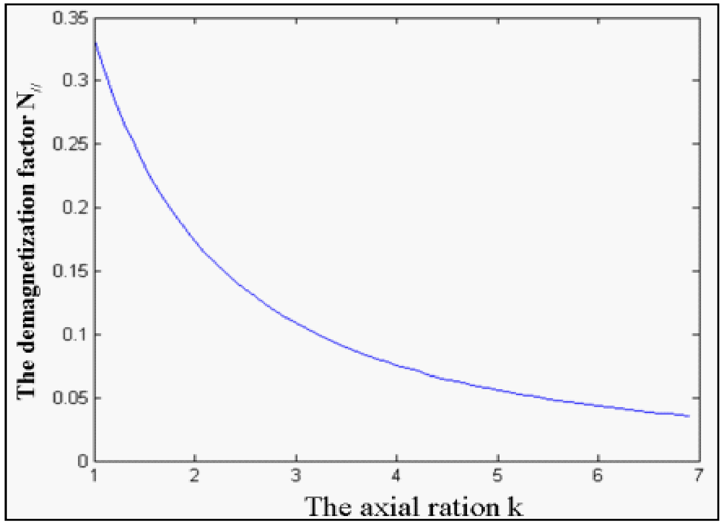
The ferrite grains and pearlite colonies alignment along the magnetic field
Zhang YD et al. J Mag Mag Mater, 2004



Schematic illustration of nucleation of ferrite
at austenite grain junctions along the magnetic field direction

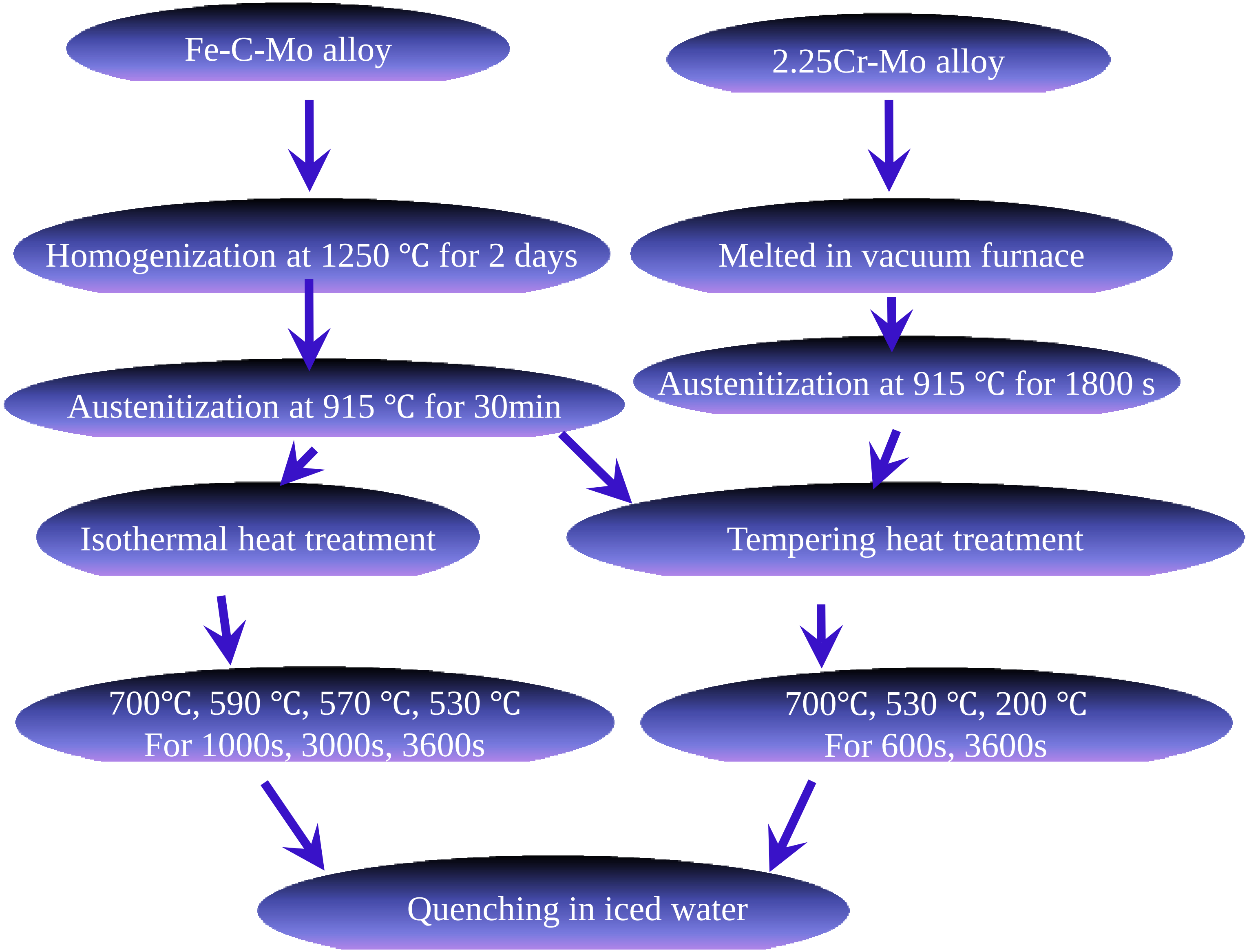


The schematic diagram of the prolate ellipsoid



The variation of demagnetizing factor
with the aspect ratio k of a prolate ellipsoid

Heat Treatment Equipment



Summary Ⅰ

◆ **The precipitation of M_6C resulted from the remarkable reduction of the magnetic Gibbs free energy.**

◆ **The substitutional solute atom concentration change in high magnetic field was mainly attributed to the change of magnetic free energy resulted from the magnetization differences of Fe and Mo atoms in each alloy carbide.**

◆ **Strong magnetic field had almost no influence on the morphology of M_6C carbide. Mininum energy principle was used to calculate the magnetic field morphology of carbide. The results show that the aspect ratio was approximately equal to 1:1, which indicates that the morphology the M_6C carbide is spherical. Actually, the Fe_3Mo_3C was appeared to be equiaxed in shape.**

Summary II

◆ The precipitation of the Fe_5C_2 and M_6C carbides were promoted by a 12-T high magnetic field at low (200°C) and intermediate temperature (530°C), respectively.

◆ The magnetic Gibbs free energy change was not only related to the magnetization but also the internal field induction of carbides. The reduction in magnetic Gibbs free energy was responsible for the promotion of specific carbides at low and intermediate temperature.

◆ There was no visible change in the precipitation sequence of alloy carbides when specimens were tempered at high temperature (700°C). This is because the alloy carbides were changed into paramagnetic phases.

◆ A 12-T high magnetic field promoted the precipitation and also increased the concentration of Fe atom of $M_{23}C_6$ or M_6C alloy carbide during martensitic tempering at 200°C, which was attributed to the reduction of Gibbs free energy caused by the high magnetic field.

◆ The concentration of substitutional solute Fe atoms in the carbide of M_6C, $M_{23}C_6$ and M_7C_3 was greatly influenced by a strong magnetic field. The higher Fe atom content in the $M_{23}C_6$ and M_7C_3 carbide makes the magnetic moment increased remarkably, which thus reduces the magnetic Gibbs free energy of alloy carbides.

◆ There was no pronounced influence on the precipitation sequence of alloy carbides when specimens were tempered at high temperature (700°C).