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Development of Resettable Alloy via Grain Boundary Segregation Engineering

Current Status of Structural Materials

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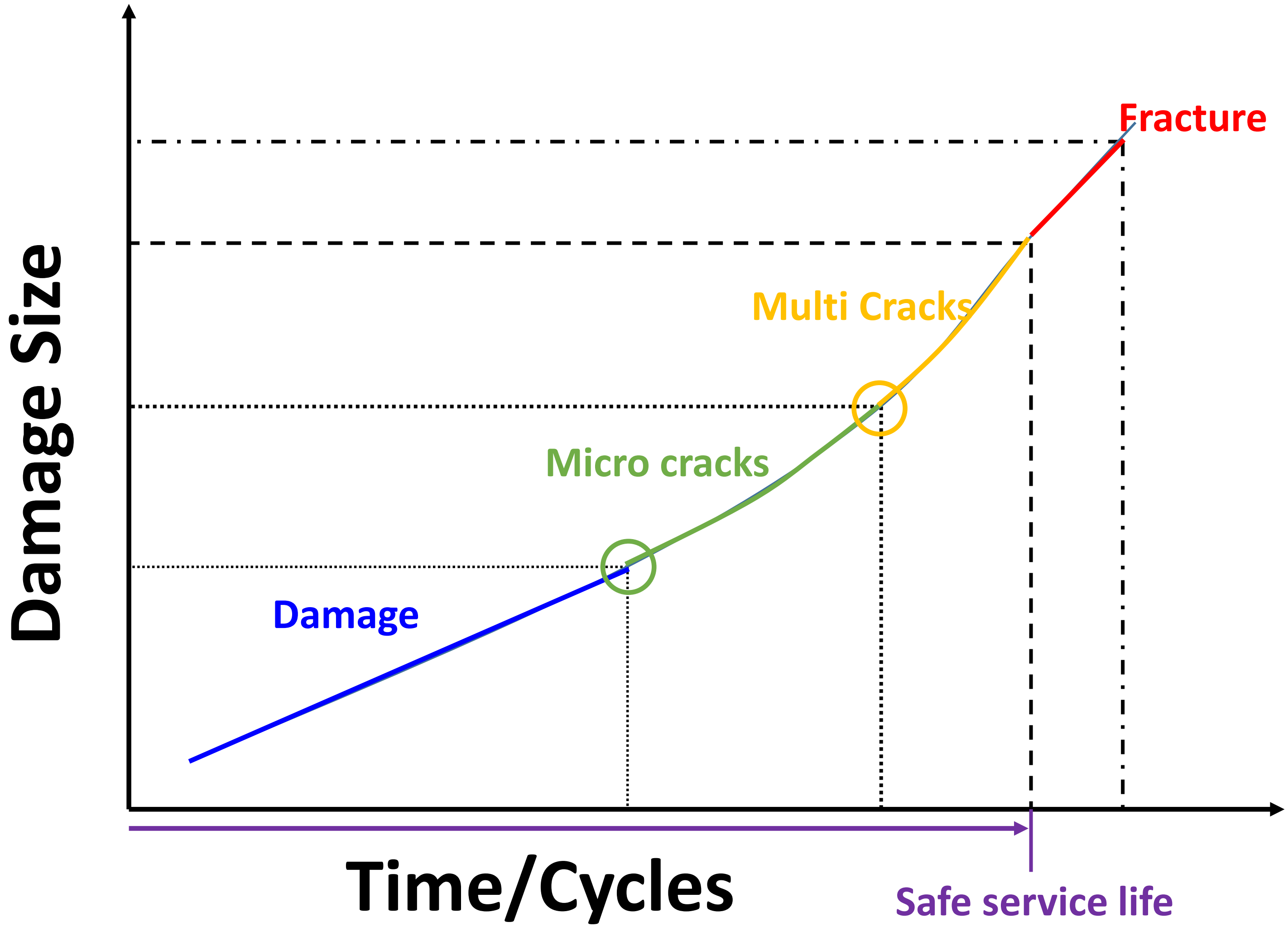
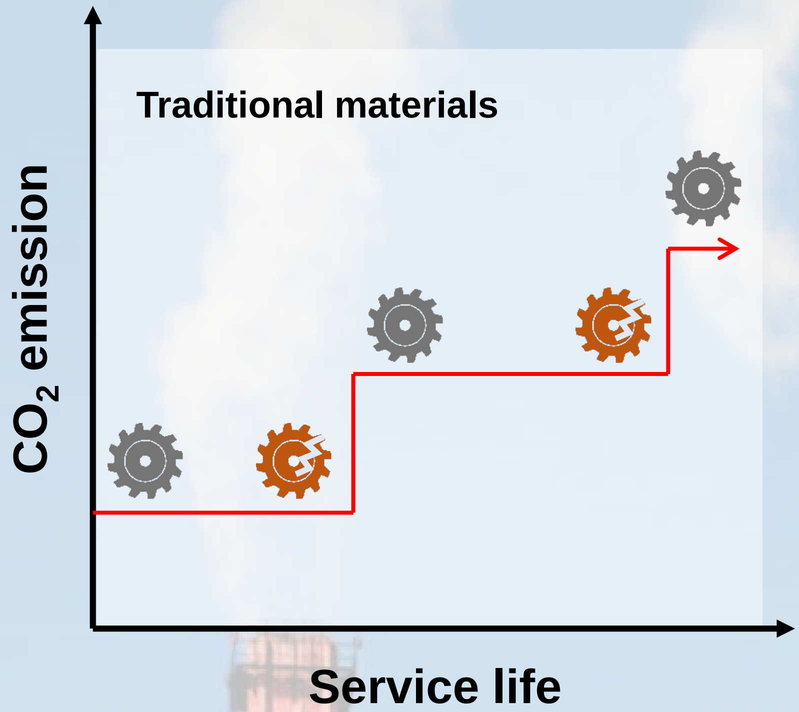
Material Damage Diagram

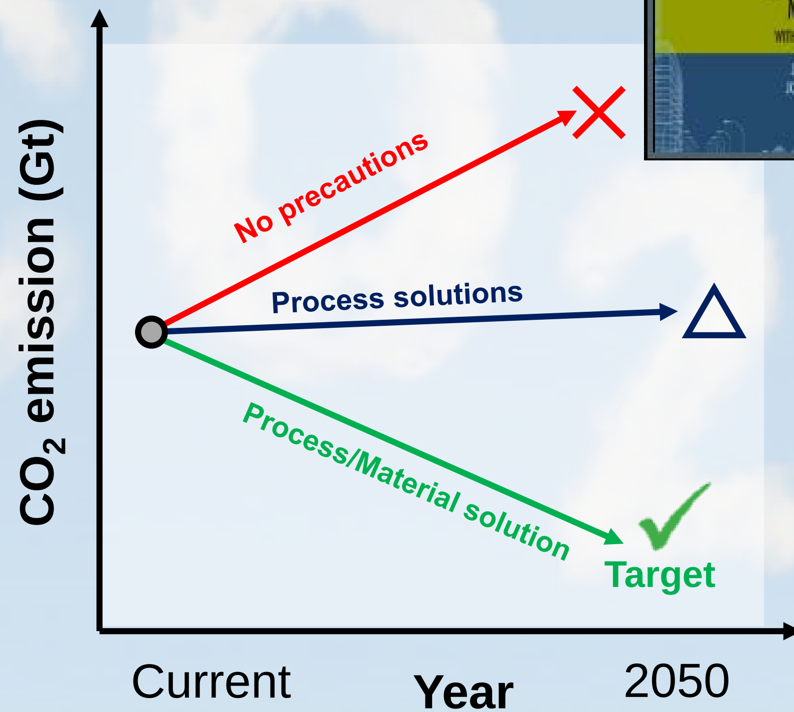


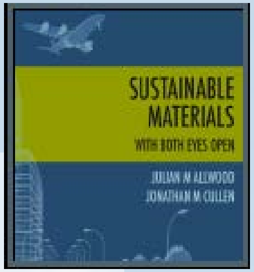
For longer life time

1. Intrinsic – development of high toughness material
2. Extrinsic – repairing material (welding..)

New challenges : Less use, Extend lifetime, Reuse!

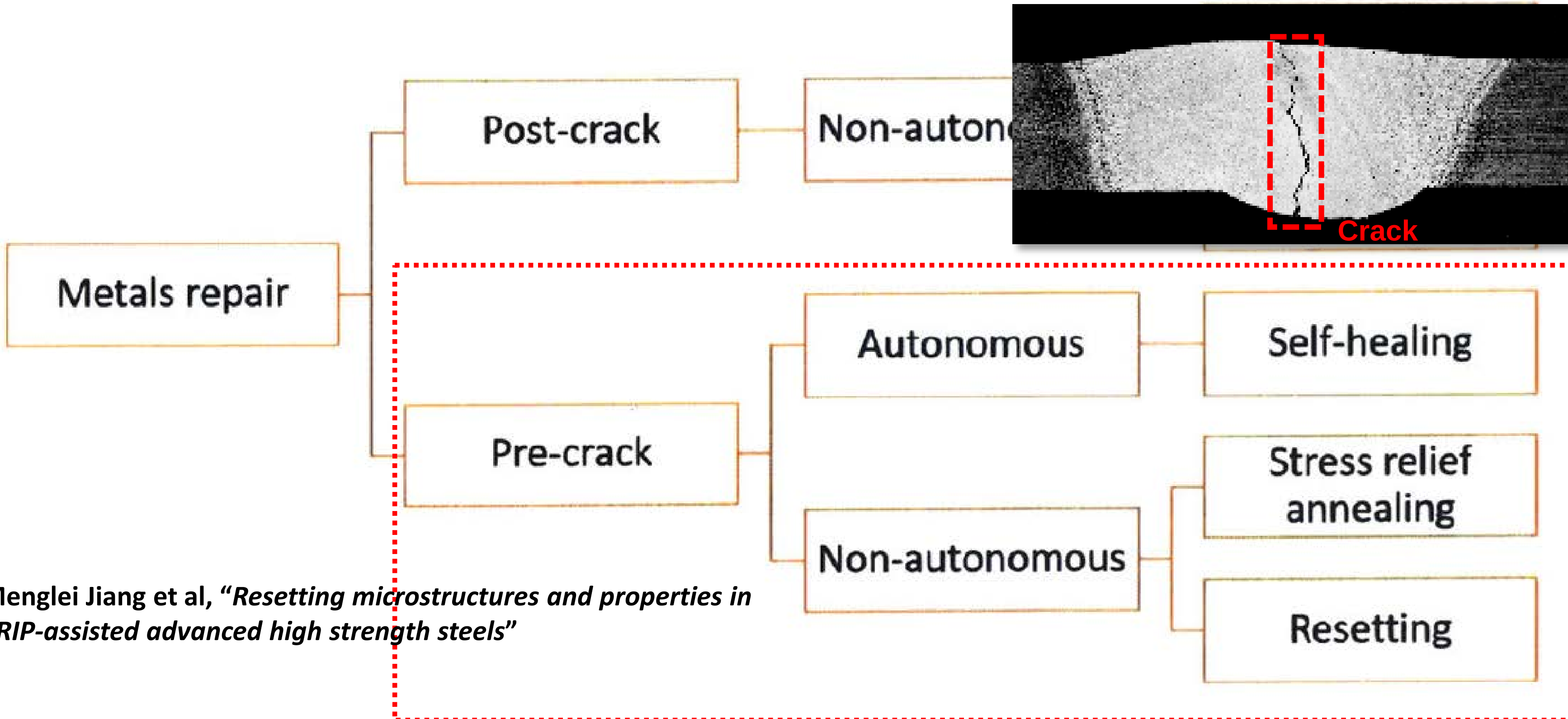






Extend lifetime, where possible, *Reuse!*

Classification of steel repairing methods

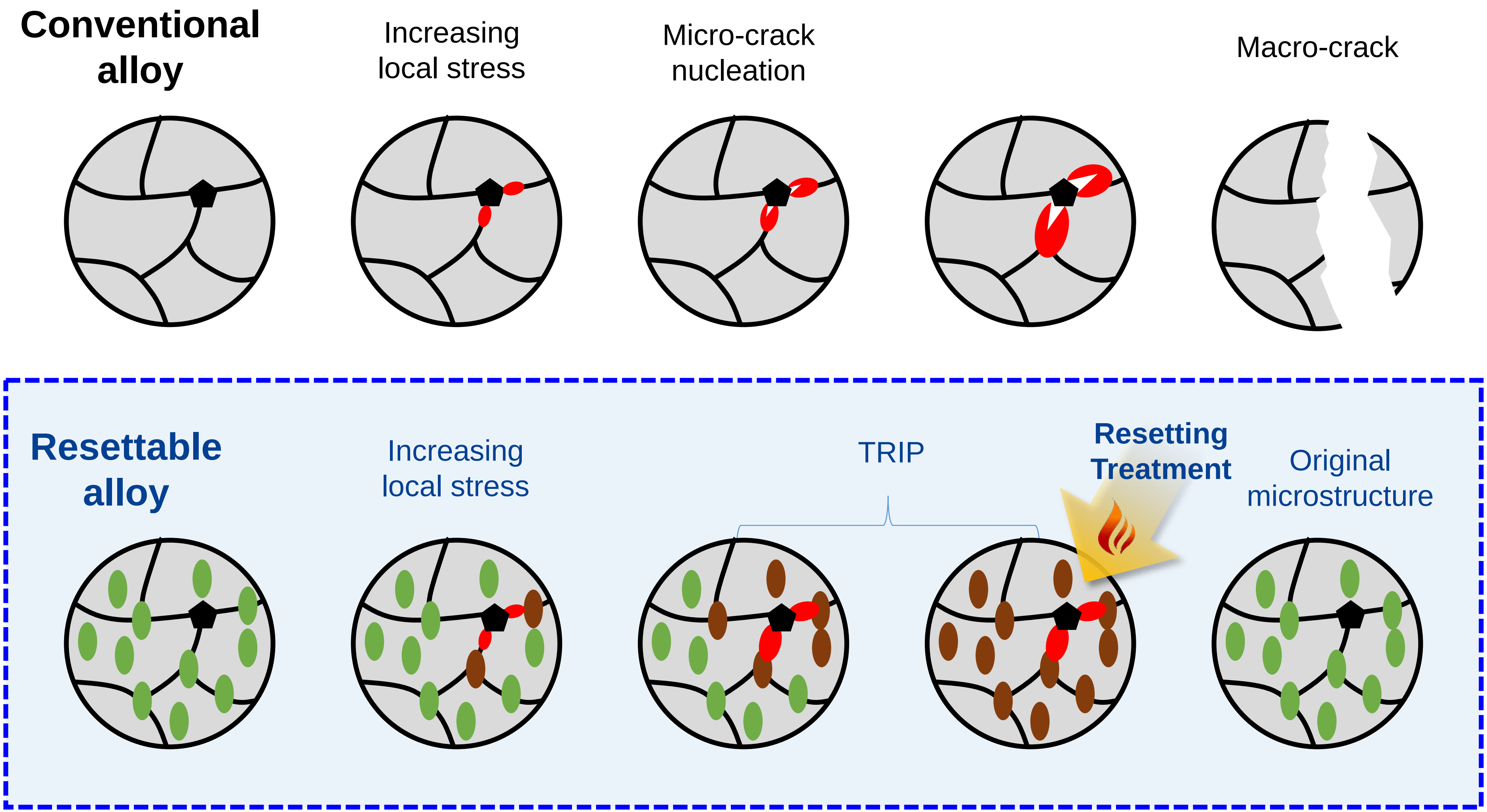


Menglei Jiang et al, "*Resetting microstructures and properties in TRIP-assisted advanced high strength steels*"

Self-healing : Autonomous / Mechanical property change

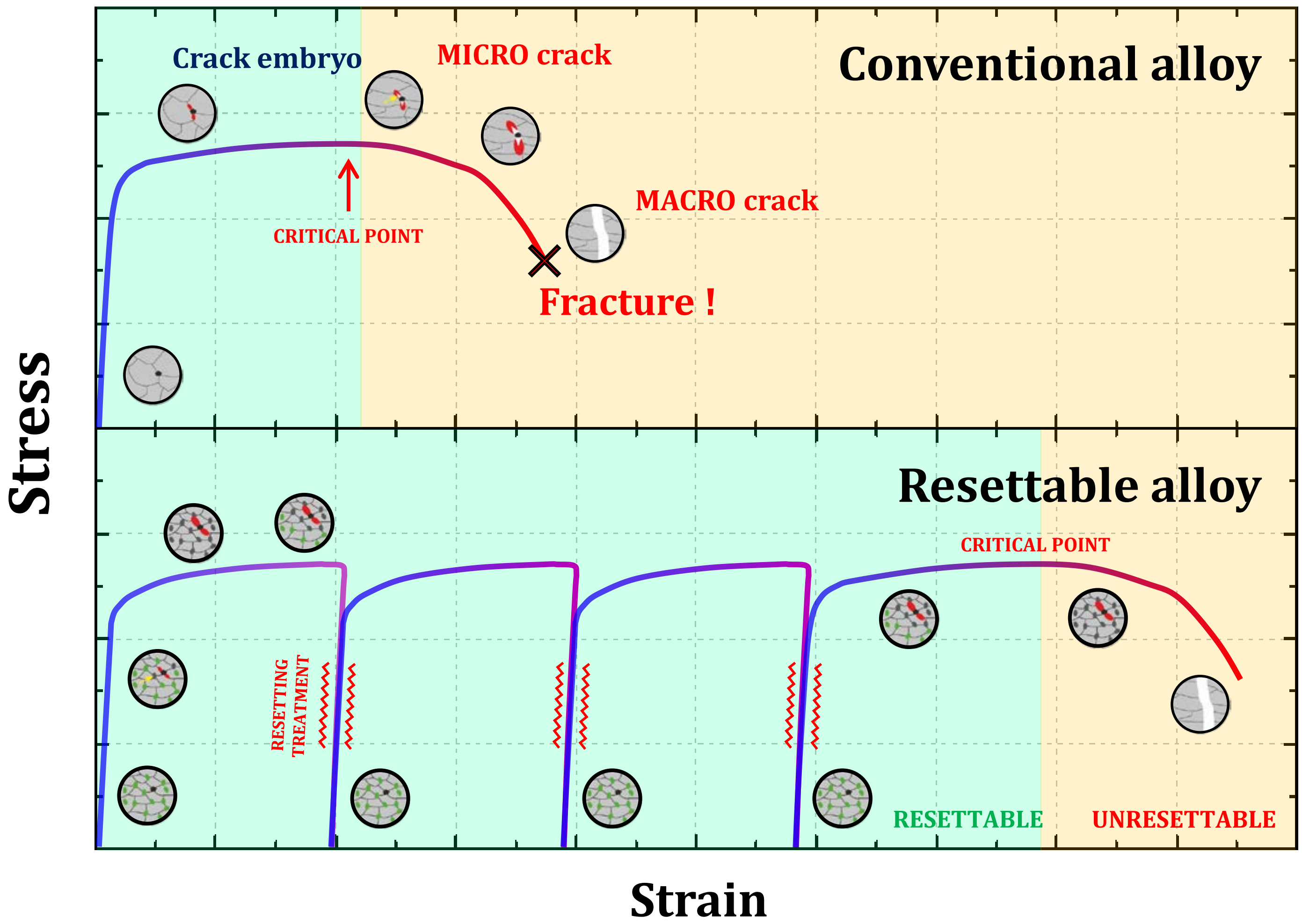
Resetting : External energy input / Mechanical property reset

New challenges : Resettable alloys!



Resetting : non-autonomic recover of original microstructure

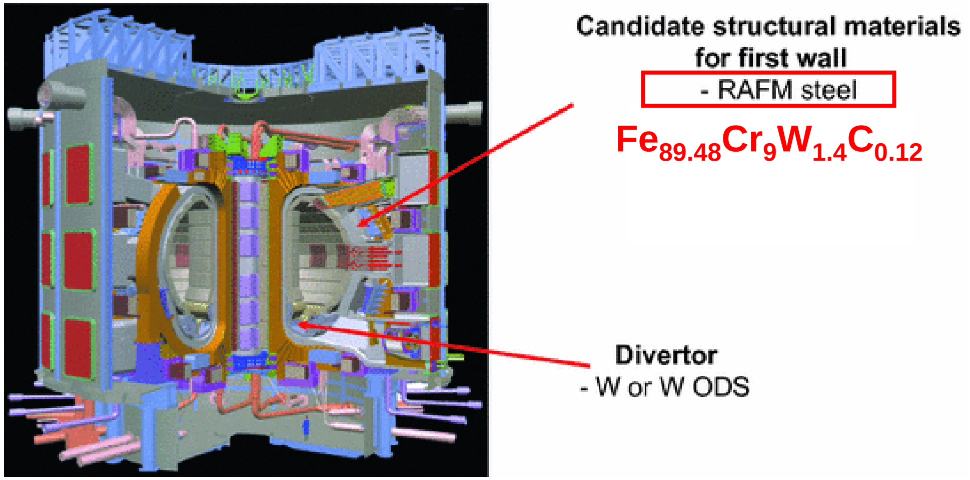
New challenges : Resettable alloys!



Resetting microstructure through resetting treatment!

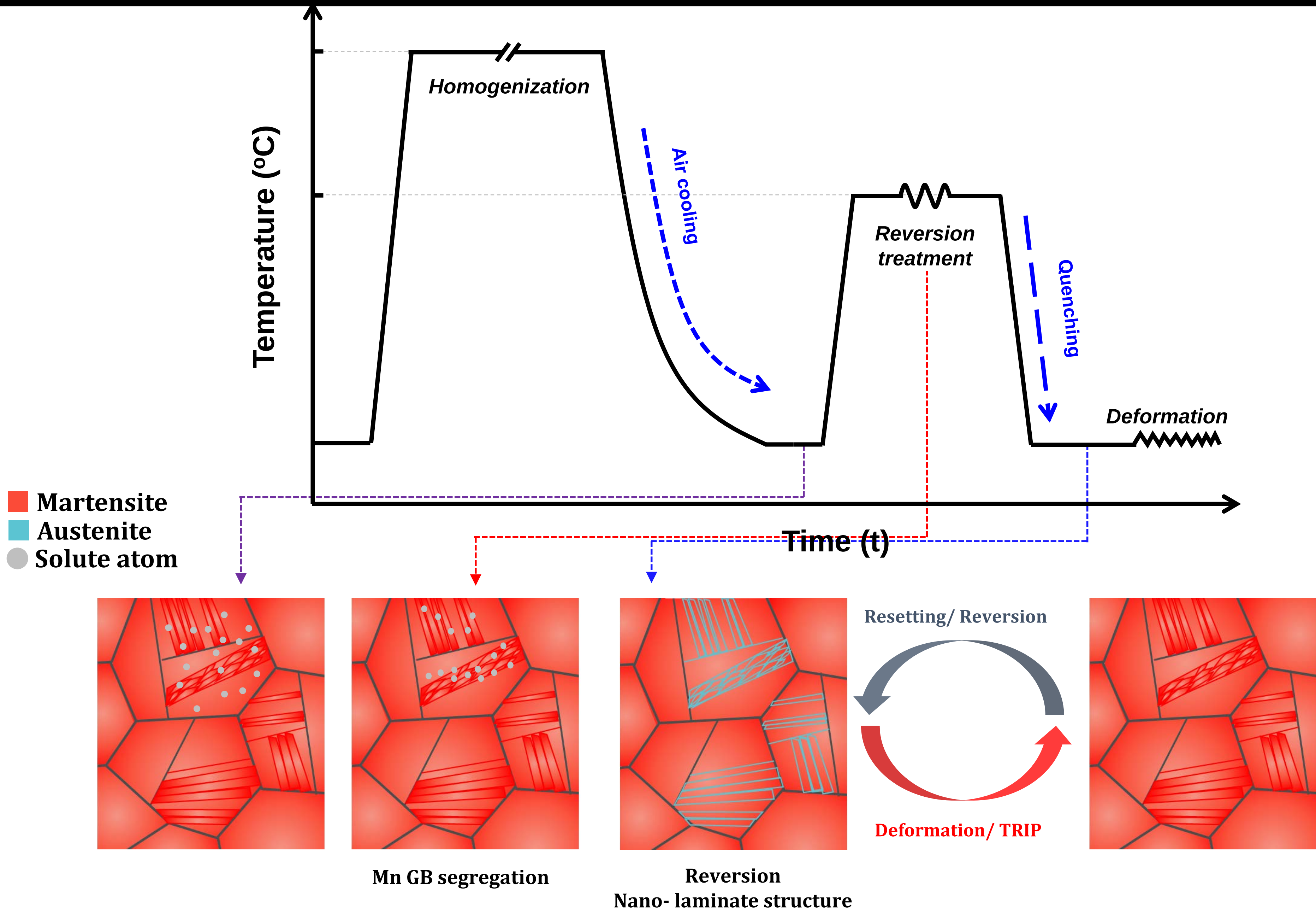
Model system: 9Cr steel

1. High toughness
2. High impact resistance
3. Relatively cheap than stainless steel
4. High oxidation resistance



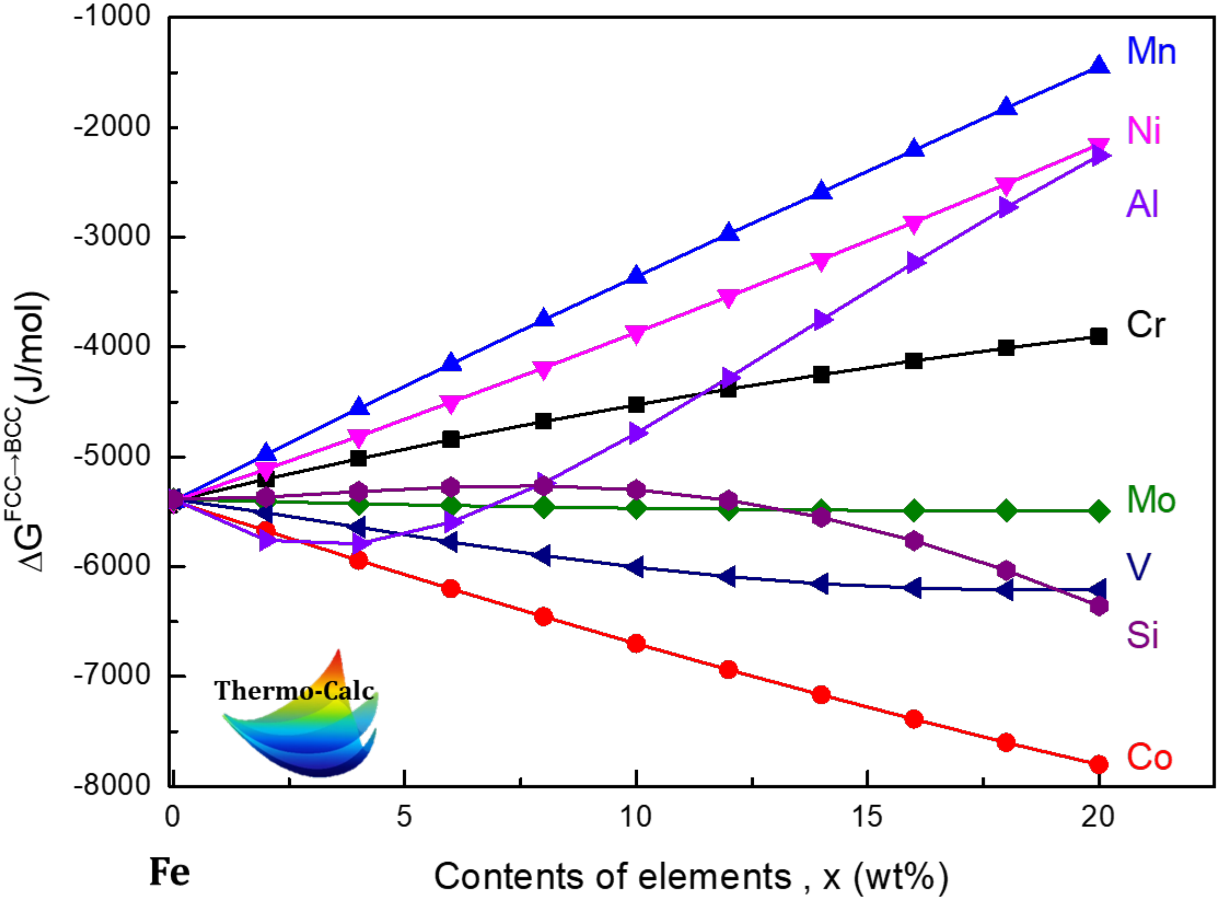
Composition of model system : $Fe_{89.48}Cr_9W_{1.4}C_{0.12}$

Resettable alloy : schematic diagram



Alloy design : Thermodynamic calculation

CALPHAD Method: Control the Austenite phase stability



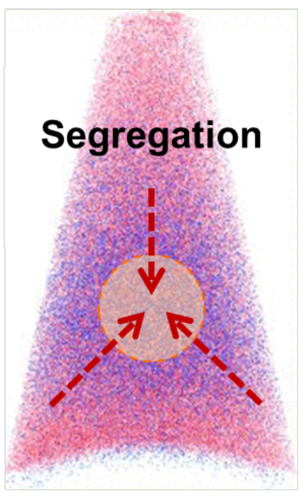
Control the Austenite phase stability by calculate $\Delta G^{FCC \to BCC}$ for each element

Alloy design considering Segregation tendency

Consideration of GB segregation tendency

Selection of alloying element considering Segregation enthalpy

$$\Delta H^{\mathrm{seg}} = \underbrace{-0.71 \times \tfrac{1}{6} \times}_{\text{Geometric term}} \Big(\underbrace{-\Delta H^{\mathrm{int}}_{\mathrm{BinA}}}_{\text{Binding E (Chemical E)}} \underbrace{- c_0 \gamma_{\mathrm{S}}^{\mathrm{A}} \Omega^{\mathrm{A}^{2/3}} + c_0 \gamma_{\mathrm{S}}^{\mathrm{B}} \Omega^{\mathrm{B}^{2/3}}}_{\text{Surface energy}} \Big) + \underbrace{\Delta E_{\mathrm{el}}}_{\text{Surface E}}$$



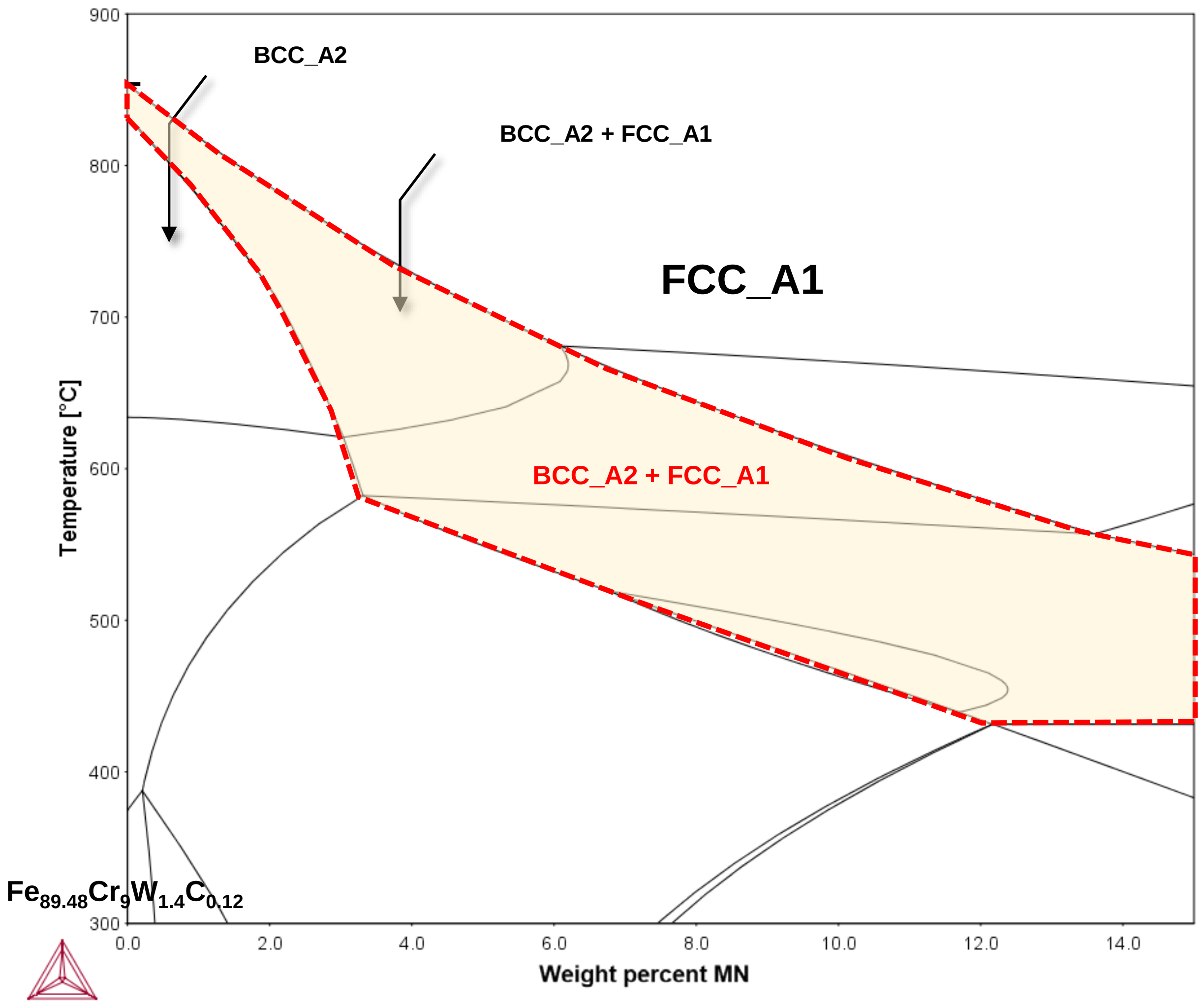
$\Delta H_{segregation}$ (J/mol)		Solvent				
		Cr	Mn	Fe	Co	Ni
Solute	Cr	-	-11652	3737	2720	-728
	Mn	15095	-	16605	13781	10005
	Fe	-1676	-16222	-	-527	-4765
	Co	-1485	-18154	243	-	-2473
	Ni	-223	-17223	2124	2237	-

Heather A. Murdoch and Christopher A. Schuh, "***Estimation of grain boundary segregation enthalpy and its role in stable nanocrystalline alloy design***", Journal of Materials Research, 28 (2013) 1628

Considering FCC Phase stability & Segregation tendency : Mn element is the best candidate

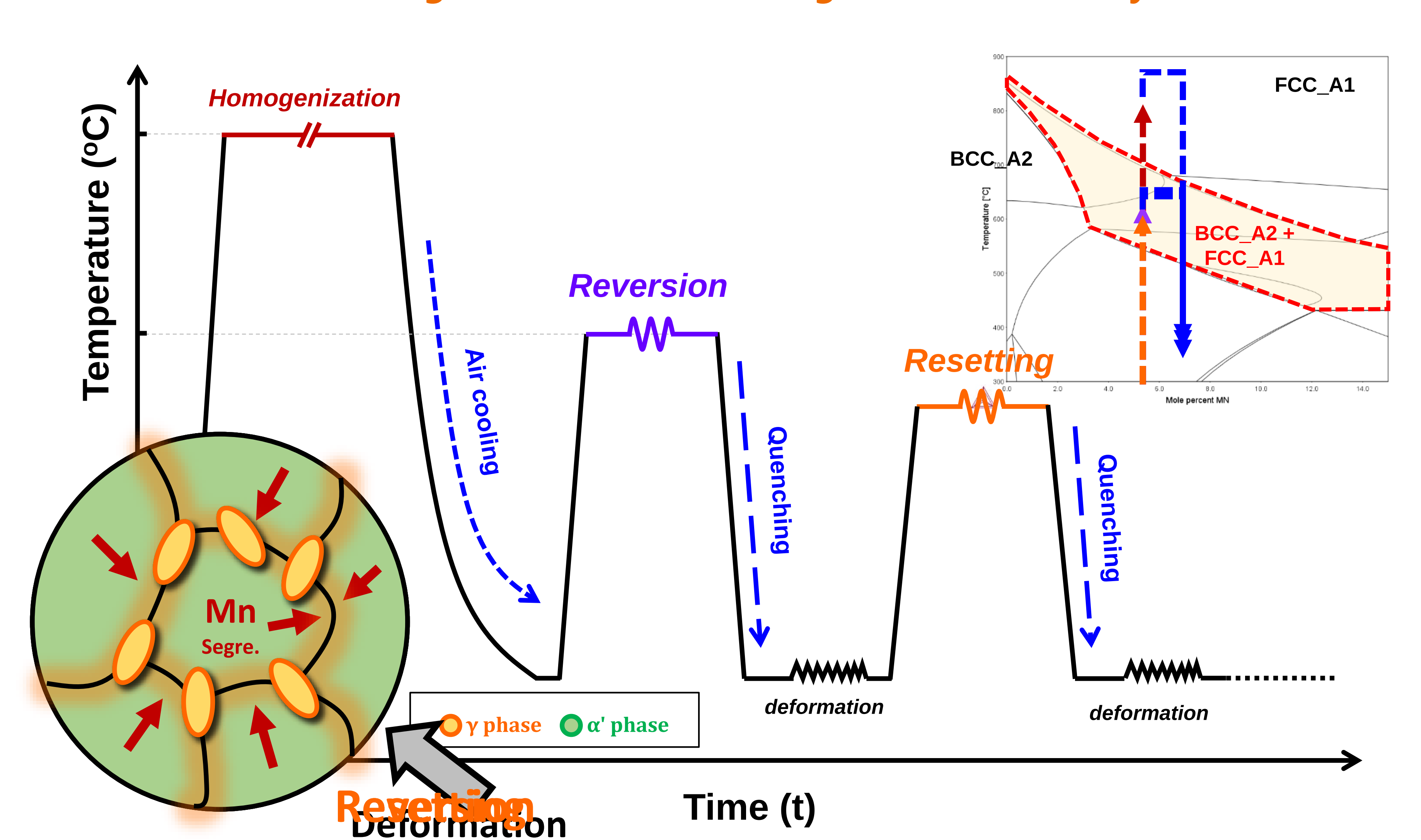
Thermodynamic Calculations for Model system

Model system: $Fe_{89.48-x}Mn_xCr_9W_{1.4}C_{0.12}$ (x=0-15 wt.%) alloys



Process and Microstructural design for Model system

Processing and Microstructural design for Resettable alloy

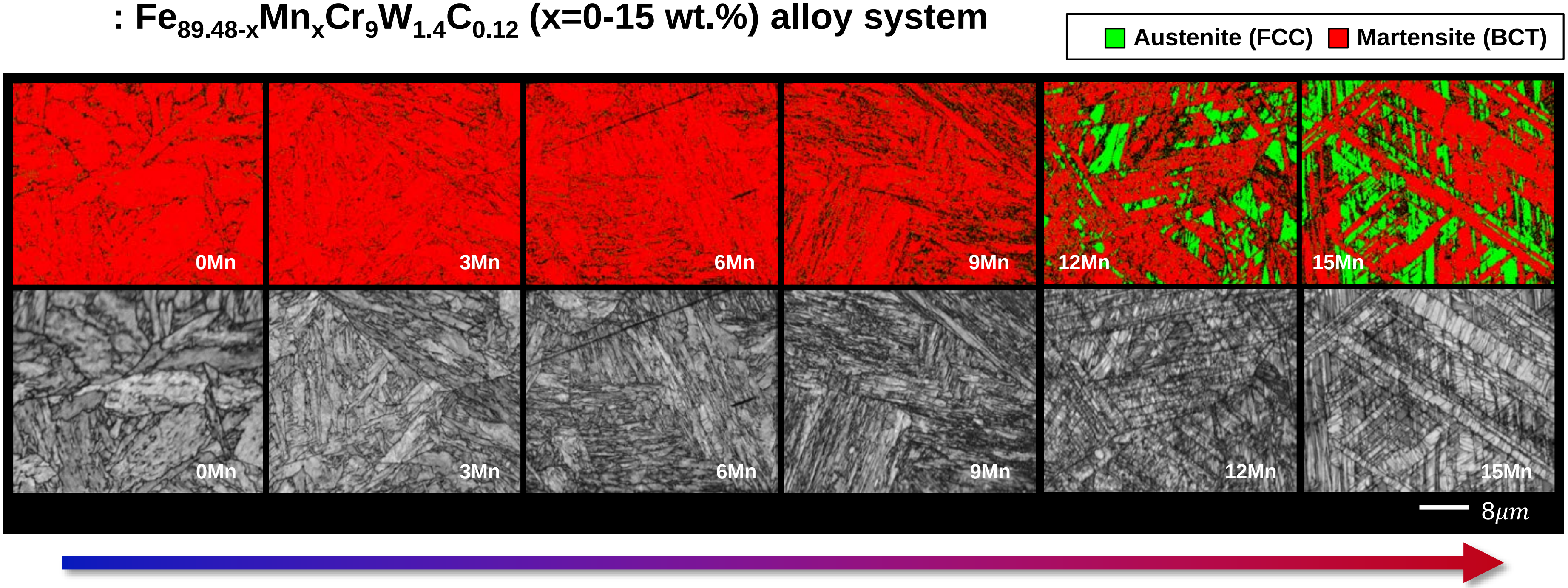


Optimization of Resettable alloy composition

EBSD analysis results : As homogenized and air cooled specimen

① Microstructural analysis for various Mn contents

: $Fe_{89.48-x}Mn_xCr_9W_{1.4}C_{0.12}$ (x=0-15 wt.%) alloy system



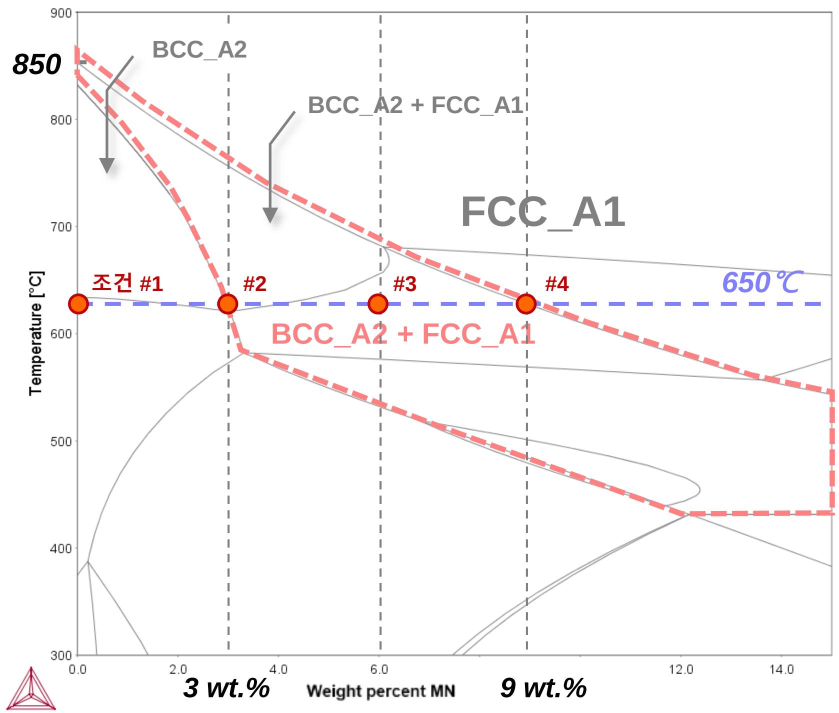
Phase stability of Austenite increase with Mn contents

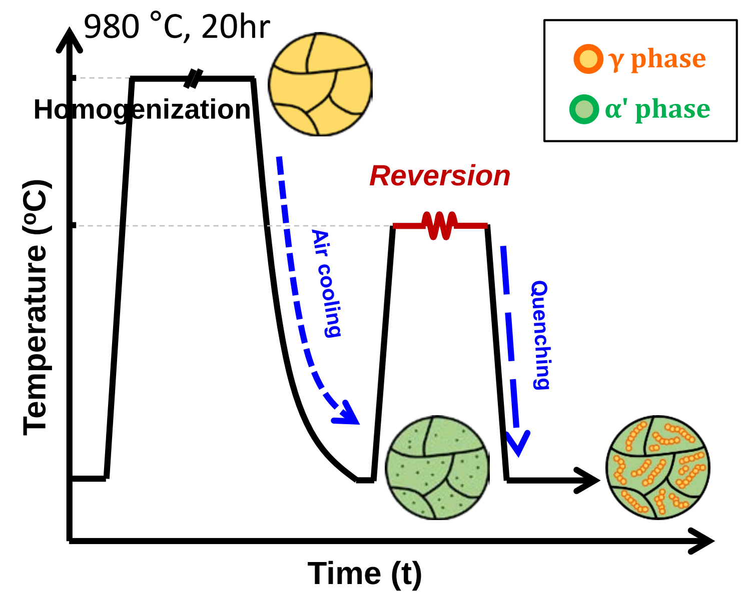
- For 0 wt.% < Mn < 15 wt.% , EBSD analysis for microstructural change
- For Mn < 9 wt.% : Fully martensite microstructure at as homogenized and air cooled state

Optimization of Resettable alloy composition

Reversion temperature selection considering phase stability

② Reversion process temperature selection using Pseudo-binary PD



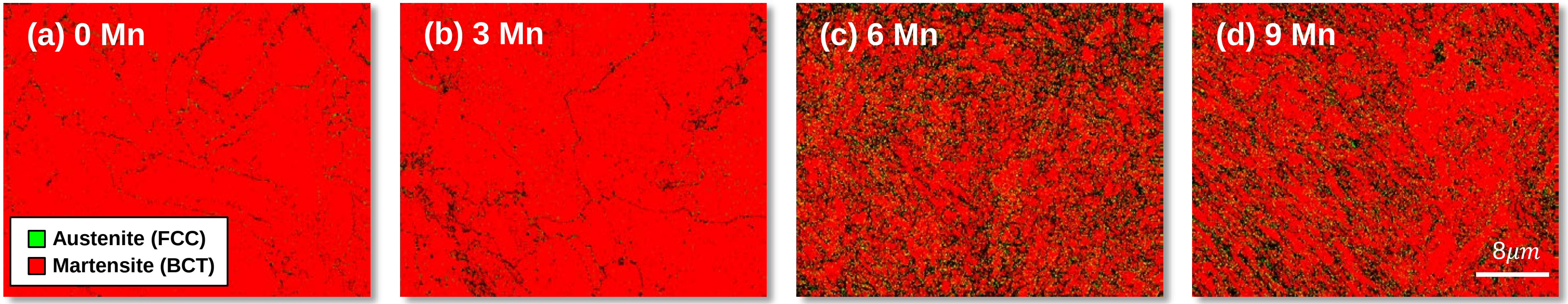


▶ For all composition, FCC/BCC co-exist at 650℃ -> Reversion temperature

Optimization of Resettable alloy composition

EBSD analysis results : After reversioned specimen

③ Microstructural analysis after the reversion process for various Mn contents



Y fraction : ~ **1%** | **~ 1%** | **~ 8%** | **~ 10 %**

Reversioned austenite phase fraction change with Mn contents changing

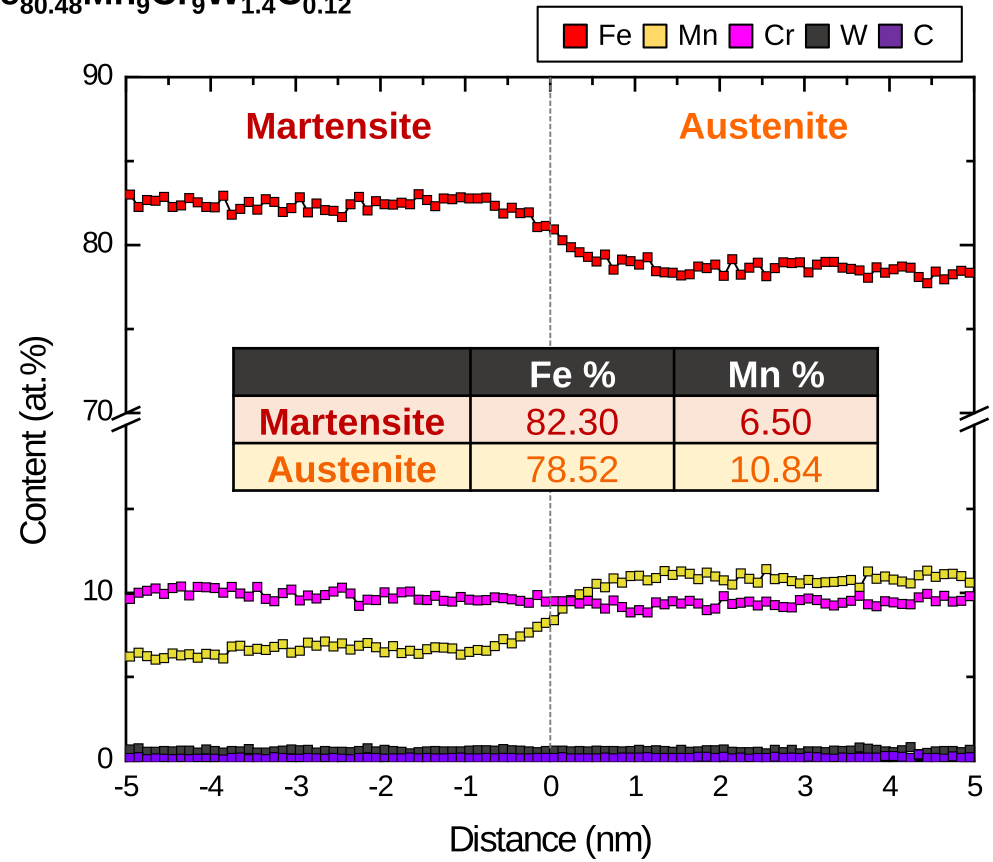
- **EBSD analysis after reversion process (650℃, 20hr)**
- **Reversioned austenite was observed for 6Mn,9Mn wt.% alloy**
- **6Mn,9Mn alloy has smaller grain size than** 0Mn, 3Mn **after reversion process**

▶ **6Mn, 9Mn alloy can be the candidate for the resettable alloy**

APT results : Austenite reversion in GB area

APT results : 9Mn wt.% specimen after reversion process(650℃, 20hr)

$Fe_{80.48}Mn_9Cr_9W_{1.4}C_{0.12}$



	Fe %	Mn %
Martensite	82.30	6.50
Austenite	78.52	10.84

Fe-rich Martensite

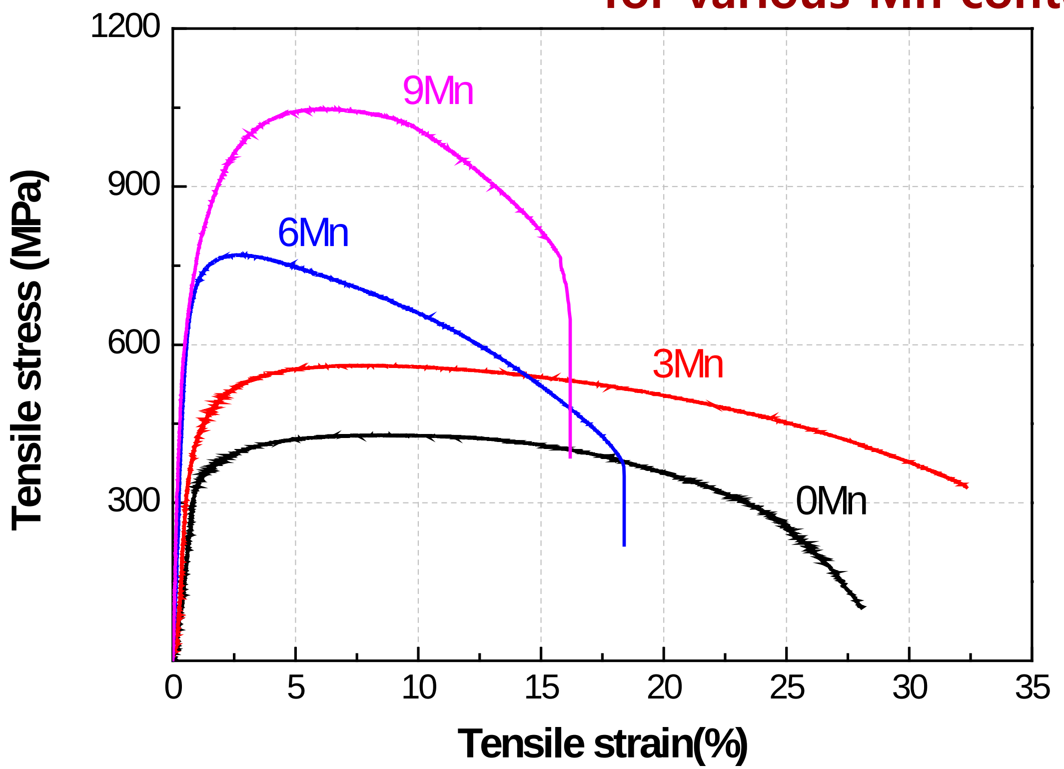
Mn-rich Austenite

▶ Y(austenite) phase / α'(marteniste) phase boundary by APT analysis

Mechanical property of Resettable alloy

Tensile test results : After reversion process(650℃, 20hr)

④ Uniaxial tensile test results after reversion process for various Mn contents



	Strength (MPa)		Elong.
	YS	UTS	ε (%)
0 Mn	344	428	28
3 Mn	396	560	32
6 Mn	655	770	18
9 Mn	633	1047	16

: $Fe_{89.48-x}Mn_xCr_9W_{1.4}C_{0.12}$

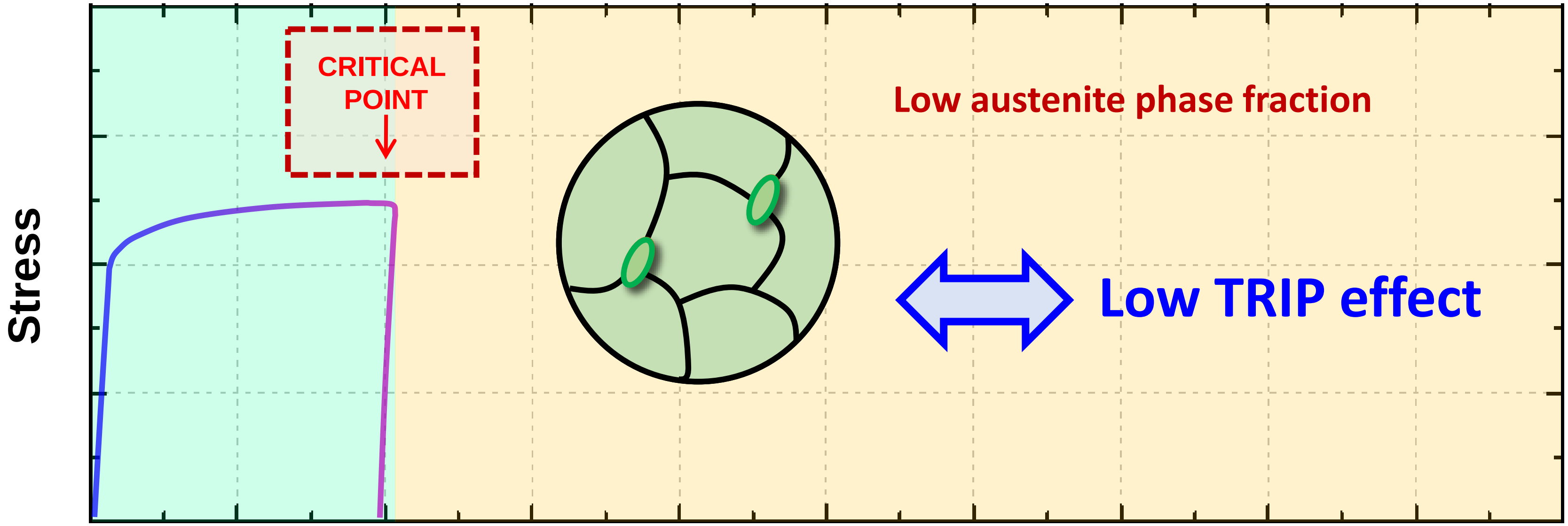
- 0Mn, 3Mn alloy has relatively low strength: grain growth during the reversion process
- 9Mn wt.% has good balance of strength and ductility

Optimization of Reversion Temperature

Maximization of austenite phase fraction for high resettability

① Optimize of reversion process condition : for maximize TRIP effect

→ Maximize phase fraction of Metastable austenite phase



Austenite phase fraction determines the critical strain reset available

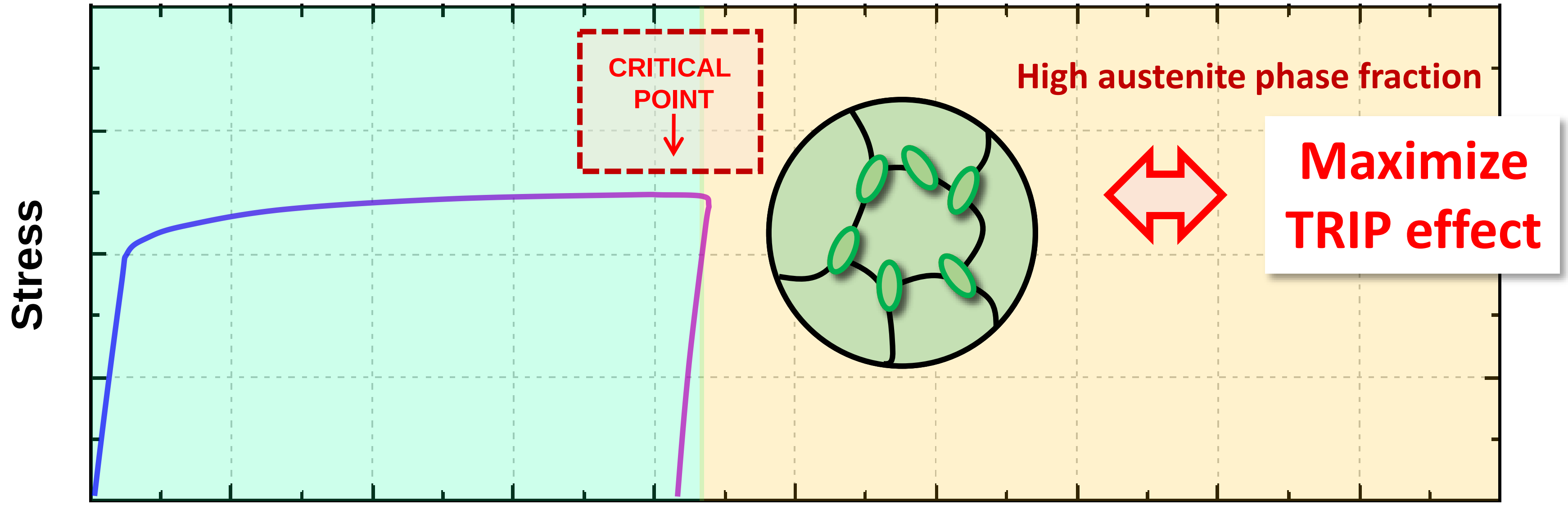
For maximizing the austenite phase fraction,
control the reversion temperature is necessary

Optimization of Reversion Temperature

Maximization of austenite phase fraction for high resettability

① Optimize of reversion process condition : for <u>maximize TRIP effect</u>

→ <u>Maximize phase fraction of Metastable austenite phase</u>



<u>Austenite phase fraction determines the critical strain reset available</u>

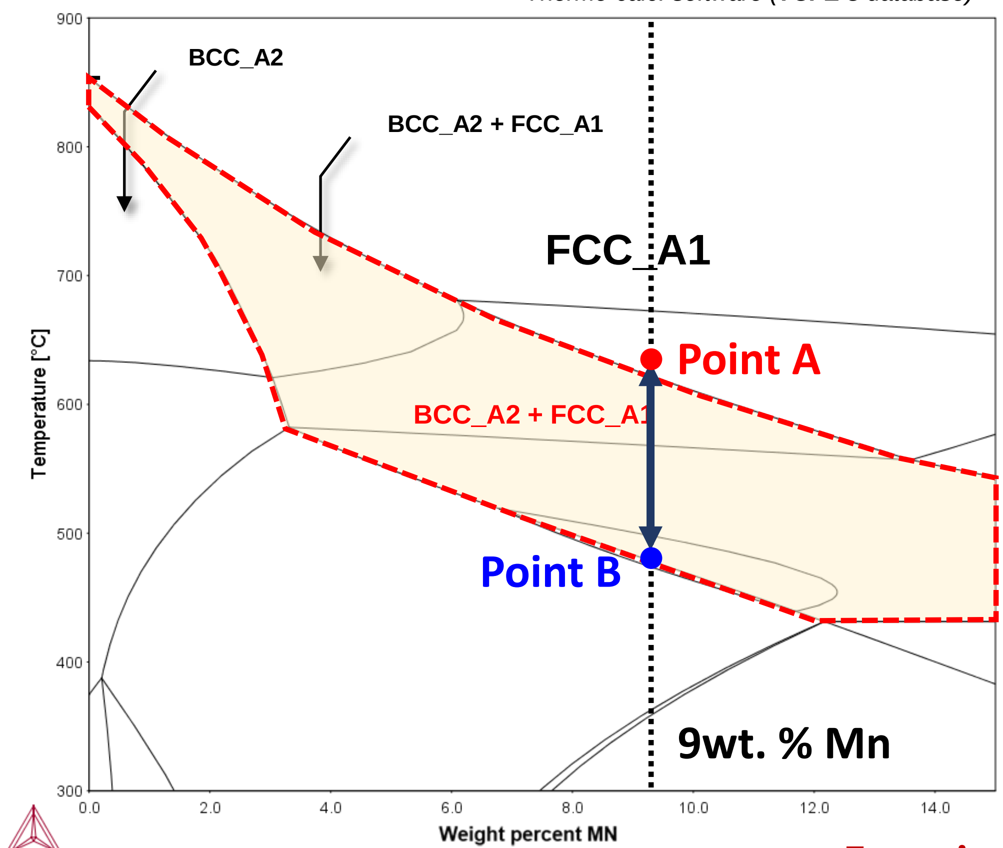
<u>**For maximizing the austenite phase fraction, control the reversion temperature is necessary**</u>

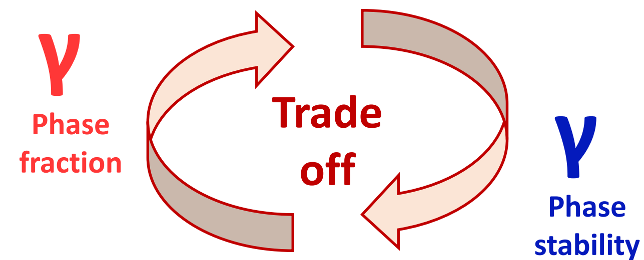
Optimization of Reversion Temperature

Phase stability – Equilibrium phase fraction trade-off relationship

① Optimizing Reversion process : γ phase stability - phase fraction trade-off

*Thermo-calc. software (**TCFE 8** database)*





	Point A	Point B
γ Phase fraction at Reversion T	100	0
γ Phase Stability	Low	High

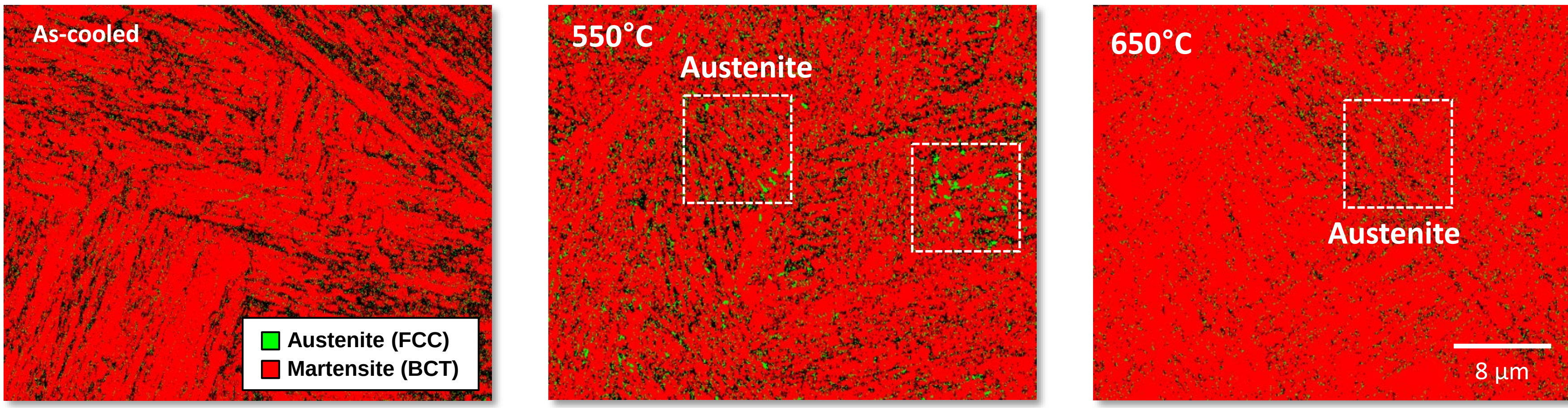
▶ Between point A and B, optimum condition For reversion process exist

Experimental procedure for obtaining optimum reversion temperature is required

Optimization of Reversion Temperature

EBSD analysis results : For various reversion temperature

① EBSD analysis for various reversion temperature : $Fe_{80.48}Mn_{9}Cr_{9}W_{1.4}C_{0.12}$



γ fraction : ~ **1%** | **22.9%** | **8.5%**

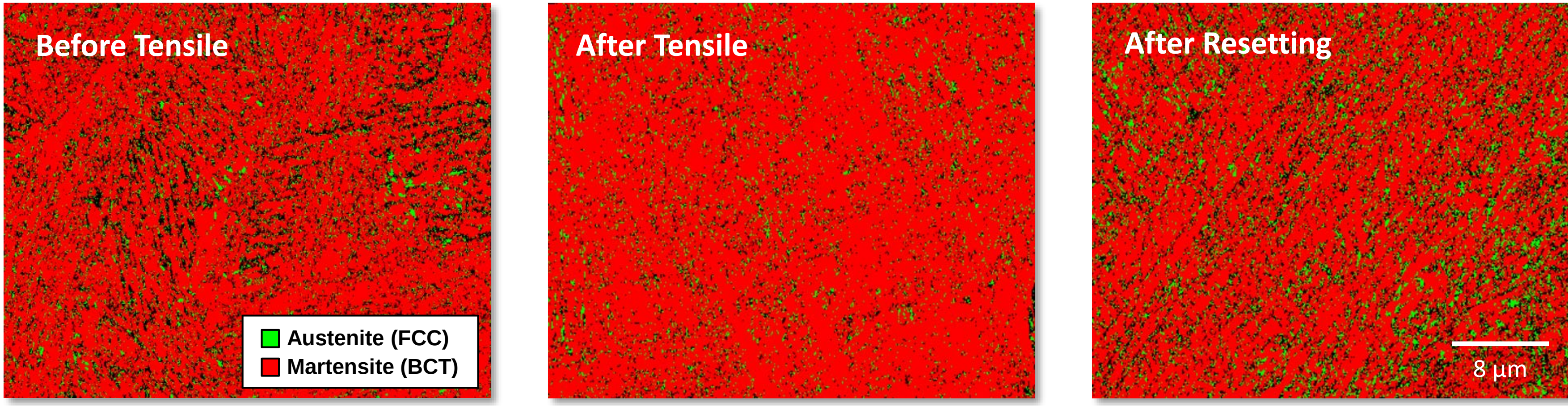
At 550℃ , maximum phase fraction of austenite was observed

▶ **Test properties of 9Mn wt.% & after 550℃ 20hr Reversion**

Resettability Test of Optimized Specimen

EBSD anlysis results : After tensile test and after resetting process

② EBSD results for before and after resetting process (550℃, 20hr)



γ fraction : **22.9 %** | **11.6 %** | **26.0 %**

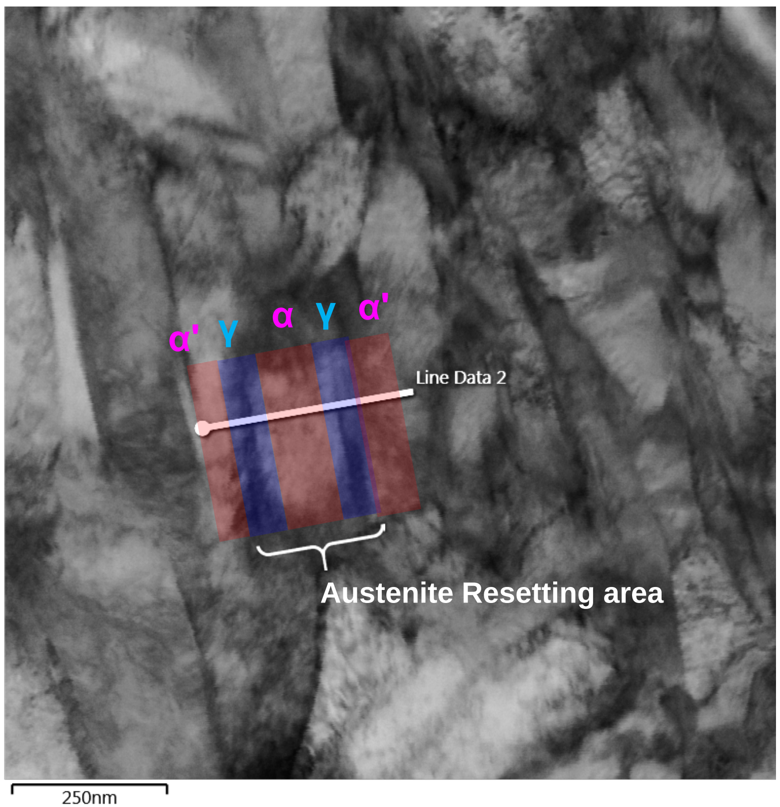
After deformation and Resetting process, austenite phase fraction recovered

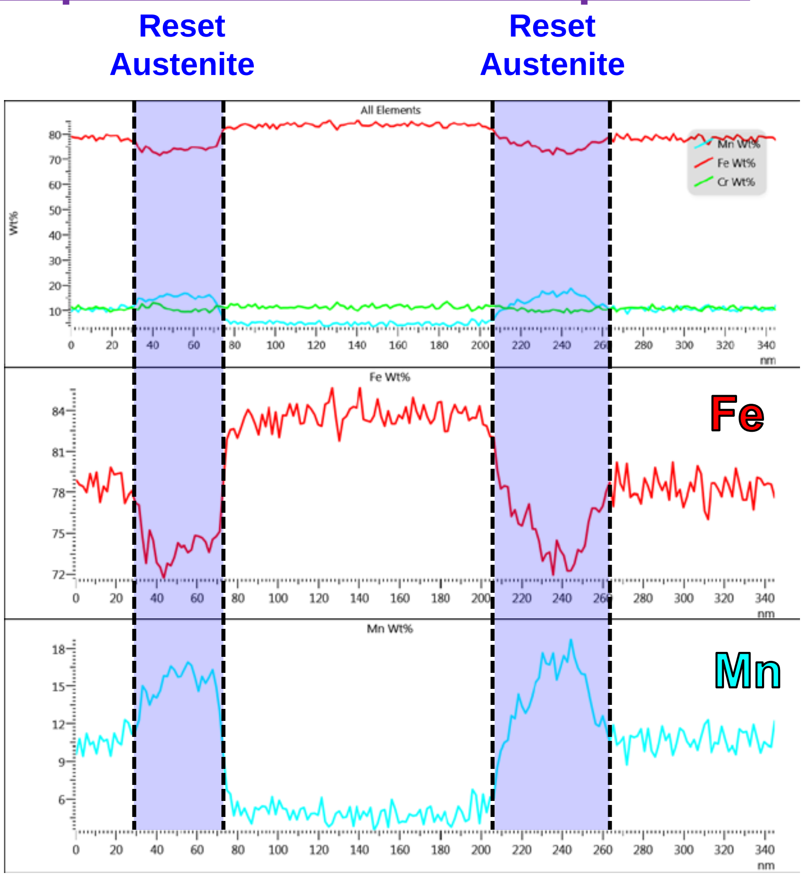
- **In the deformation stage, TRIP occurs -> austenite phase fraction reduced**
- **After resetting process, α′ phase reverse transformation to γ phase**

TEM analysis : After Reversion Process

TEM analysis : After Reversion 550℃ ,20hr)

③ Microstructure and compositional profile after reversion process



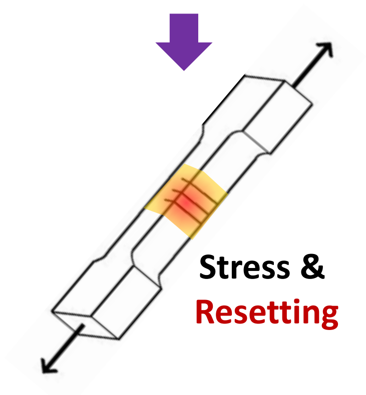


▶ Reversioned austenite after reversion : Nano-laminate structure with matrix phase

Resettability Test of Optimized Specimen

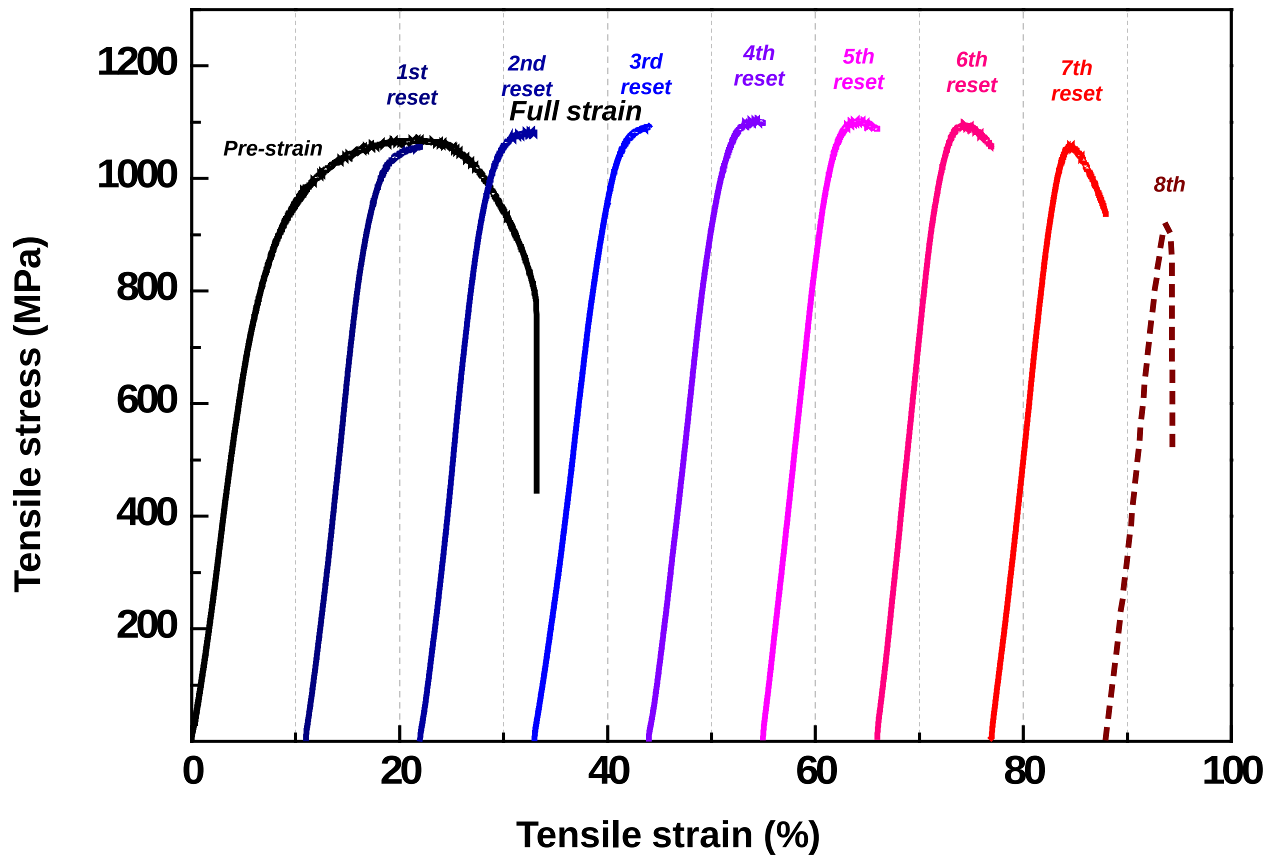
Resettability test : Deform – Resetting process cycle

Air cooling
After homogenization
at 980°C for 24h
and reversion process
at 550°C for 20 hour



(1) Pre-strain (12%)
by tensile test
for crack formation

(2) Annealing
at 550 °C for 2h



- Through Resetting Process ductility enhanced up to 3times

SUMMARY

Enhancing and Resetting Mechanical Property of 9Cr steel by Segregation Engineering

- **Considering segregation tendency and phase stability, we could make austenite-martensite nano-laminate structure in 9Cr steel.**

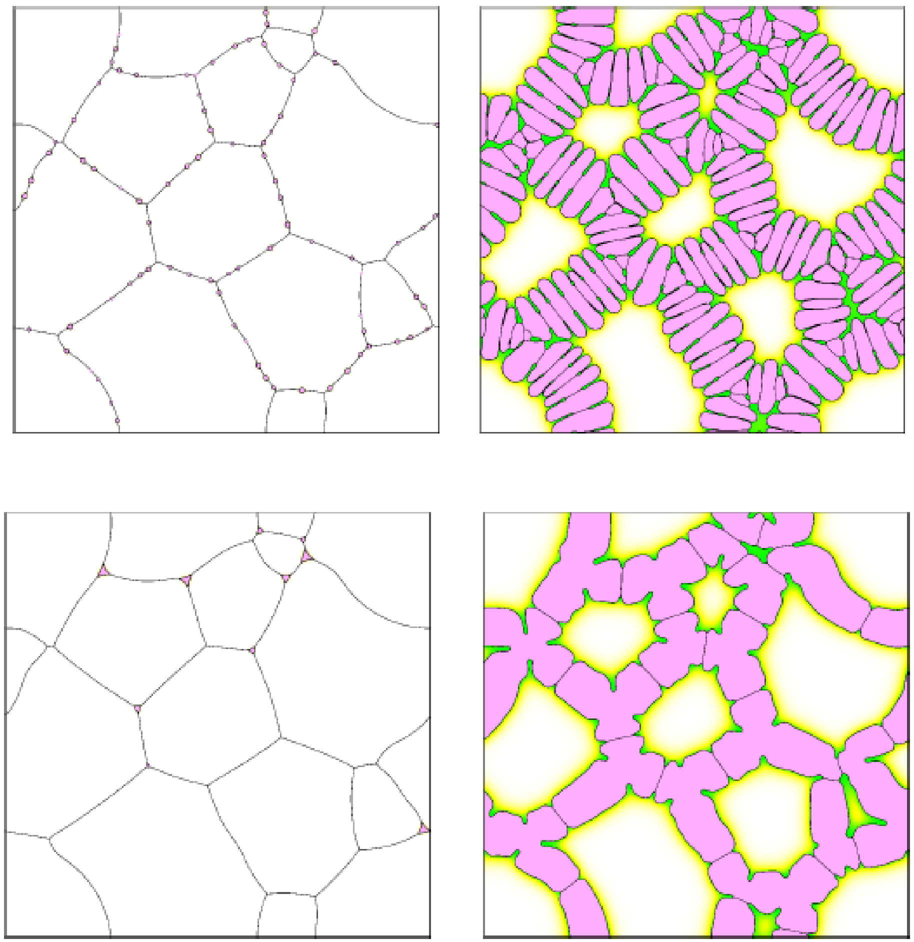
- **And then we optimized the reversion temperature experimentally, considering the phase stability and equilibrium phase fraction trade-off relationship.**

- **Through these two steps, we could develop the mechanical property resettable alloy with high-strength and good ductility balance.**

- **These alloy design guideline can be further adaptable for other various type of martensite matrix based alloys**

Future work

Alloy and processing design via PFM simulation



Advantages of PFM simulation

1. Non-equilibrium and diffusion controlled moving interface calculation
2. GB segregation calculation considering GB interface energy
3. Prediction of final microstructure considering kinetic problems

Future work

Alloy and processing design via PFM simulation

Necessity of PFM simulation in this study

GB segregation occurs in very small region
-> TEM, APT analysis is required for one data point
(Fixed composition and processing)

Through PFM simulation (with customized database)

Can predict the final microstructure of various composition and reversion temperature

-> Alloy design & processing design

Segregation engineering

Trial & error research

↓

Alloy design guideline for segregation engineering

Future work

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Segregation engineering enables nanoscale martensite to austenite phase transformation at grain boundaries: A pathway to ductile martensite

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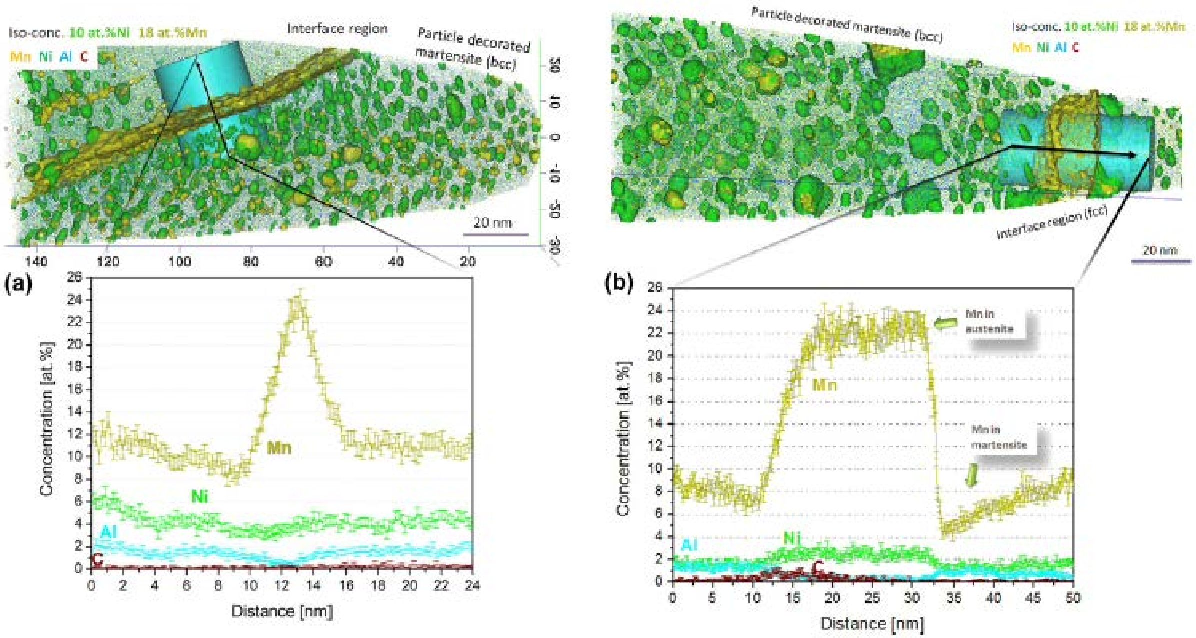

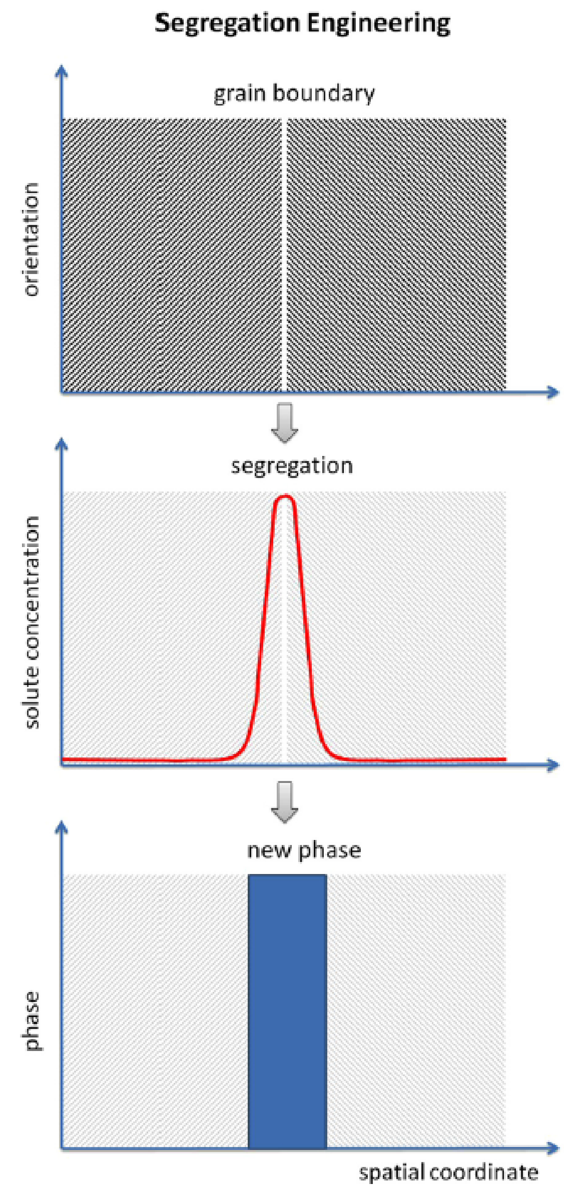

Final Goal of Research

Guideline for designing resettable alloy

For $Fe_{89.48-x}Mn_xCr_9W_{1.4}C_{0.12}$ (x=0-9 wt.%) system

Input

- x (Mn wt.%)
- T (reversion temperature)
- t (reversion time)

PFM simulation →

output

- Reversion occurs?
- Concentration profile (GB, Bulk)
- Grain size
- Austenite Phase fraction

Thank you for your kind attention

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