Heat resistant materials
&
Creep behavior

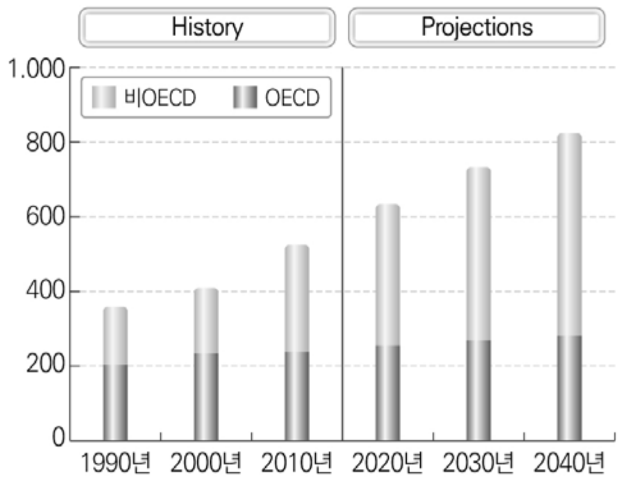
Min-Gu Jo

Contents

- Thermal power station & Heat resistant materials
- Creep deformation
- HEA for Creep-resistant material

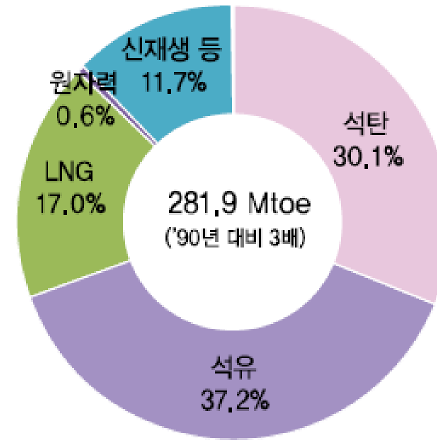
❖ Energy consumption & Thermal power station

- **IEO Energy consumption prospect**



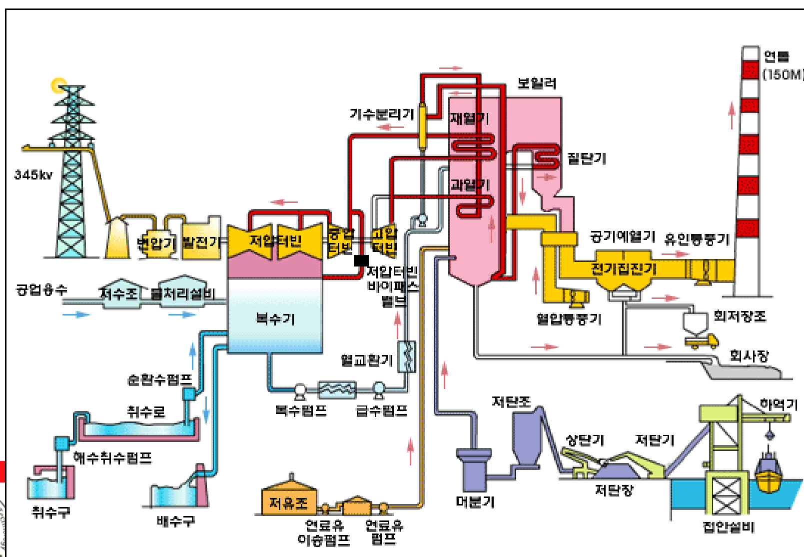
International Energy Outlook 2014

- **'14 Korea 1st Energy supplement ratio**



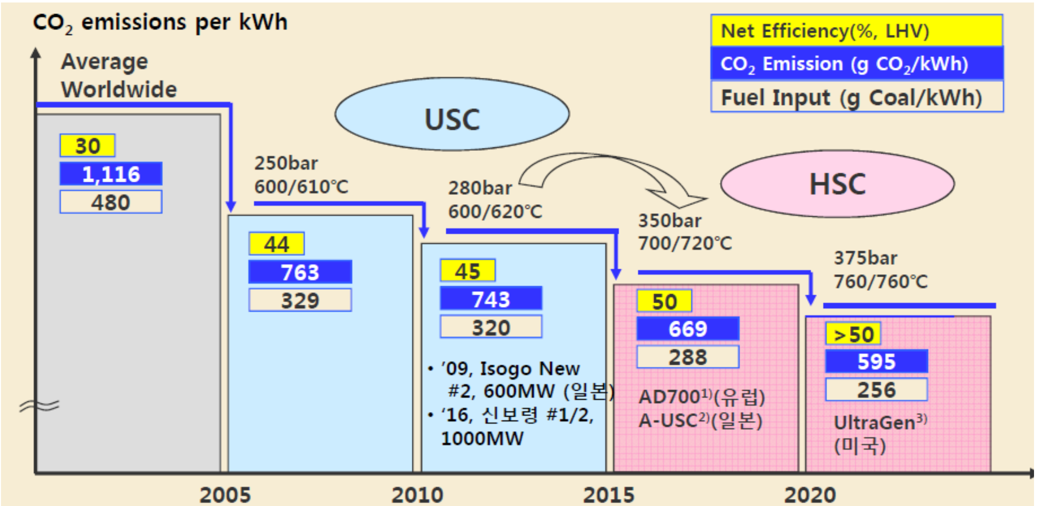
2015 Korea Energy Handbook

- **Thermal power station**



- **CCT (Clean Coal Technology)**
  - → HELE coal technology (High Efficiency Low Emission coal technology)
  - → CCS(CO_2 Capture & Storage)

❖Coal thermal power station & Heat resistant materials



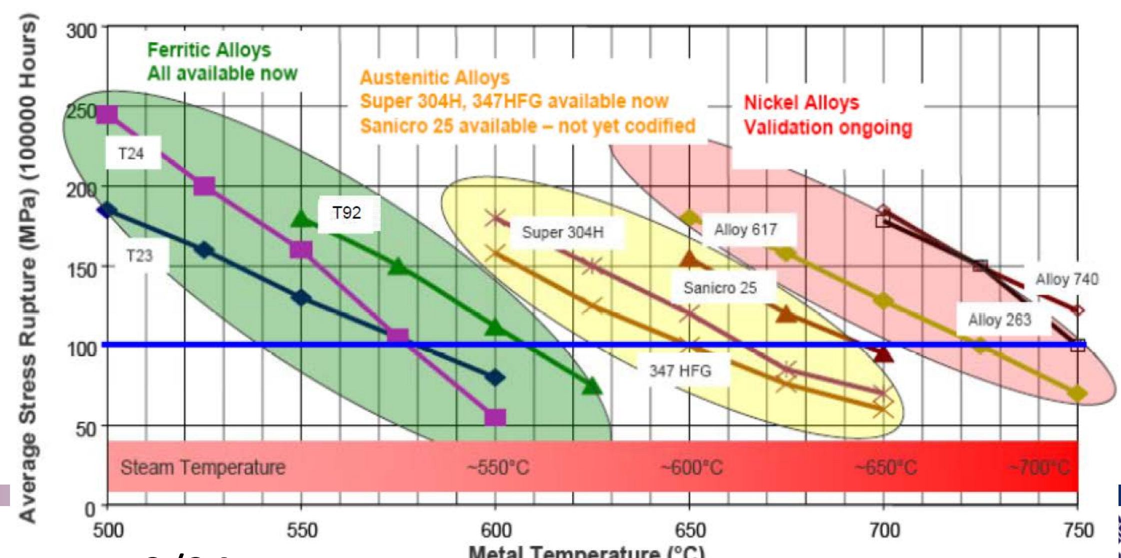
SC(Supercritical)
: 538℃↓
USC(Ultra-supercritical)
: 566℃↑
HSC(Advanced-USC)
: 704℃↑

T↑ → Efficiency↑ → CO_2 emission↓

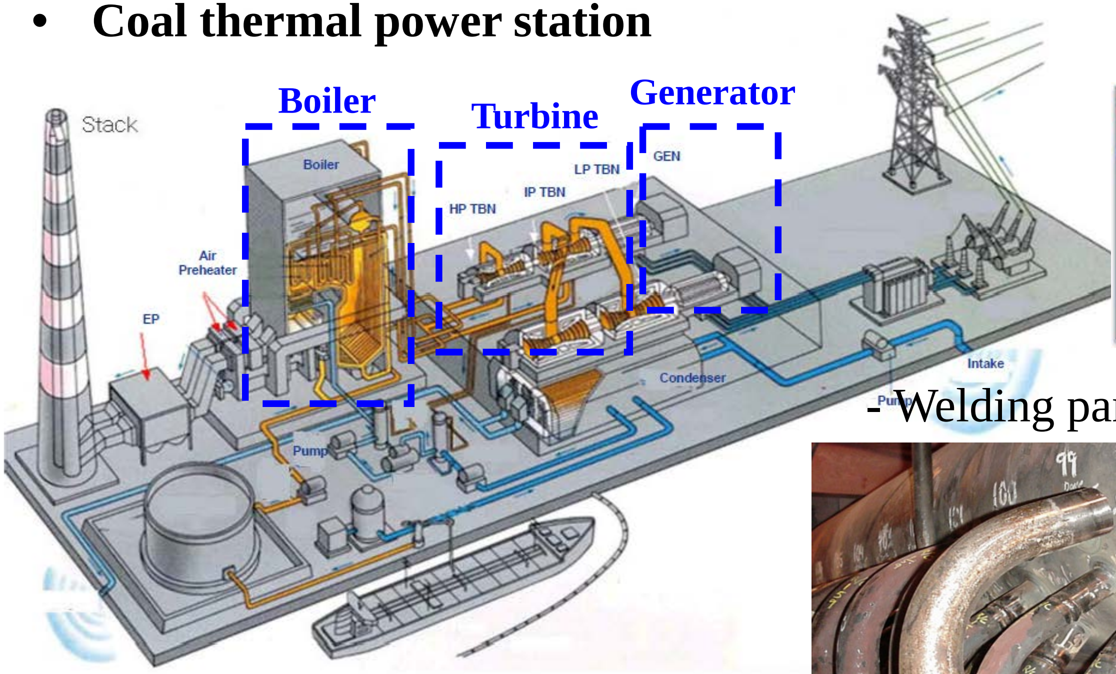
- Current state of Korea

- SC → USC
- 6000 ton CO_2/MW
- 30% efficiency (ave)

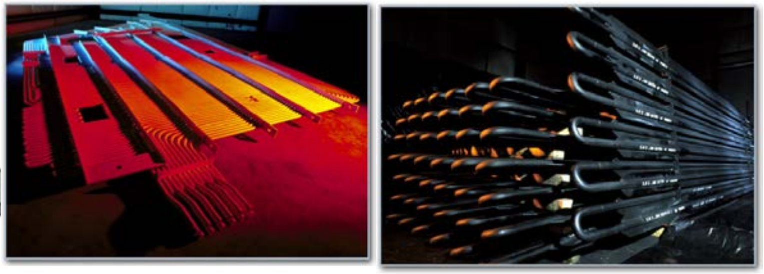
- **Heat resistant materials**



- **Coal thermal power station**



- Boiler (tube, pipe)



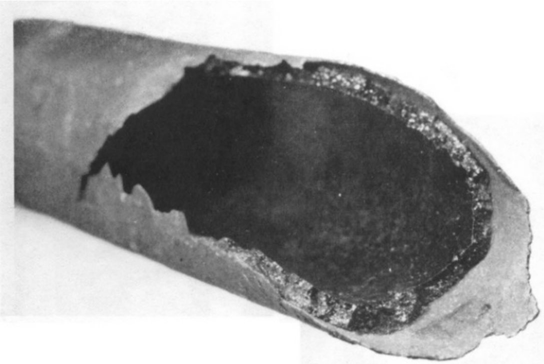
- Welding part

- Turbine

- Bending part

- Corrosion

- Oxidation

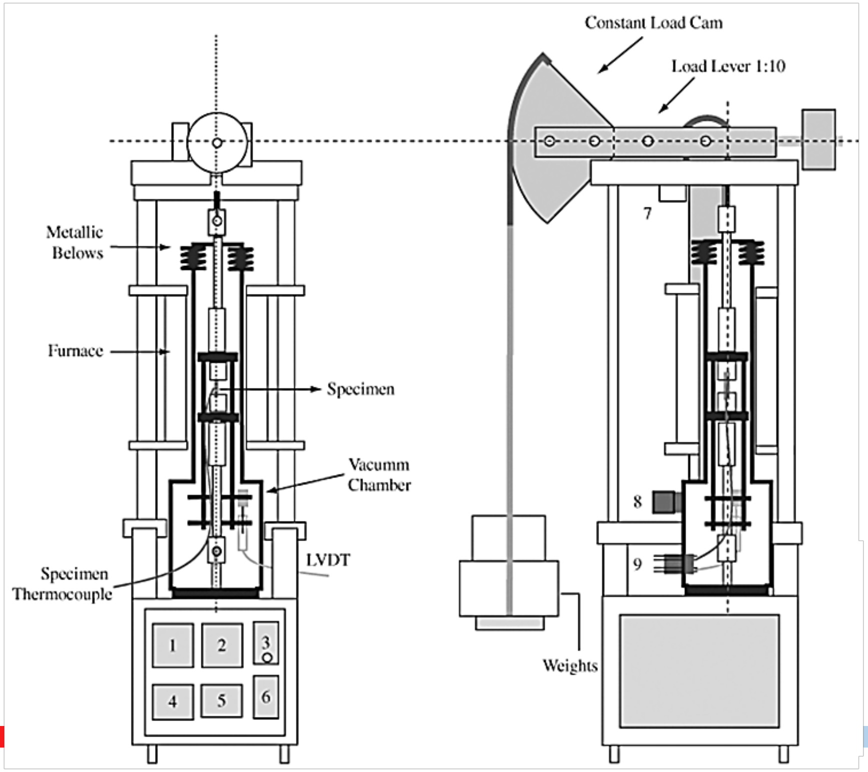


❖ Creep

- **Definition**

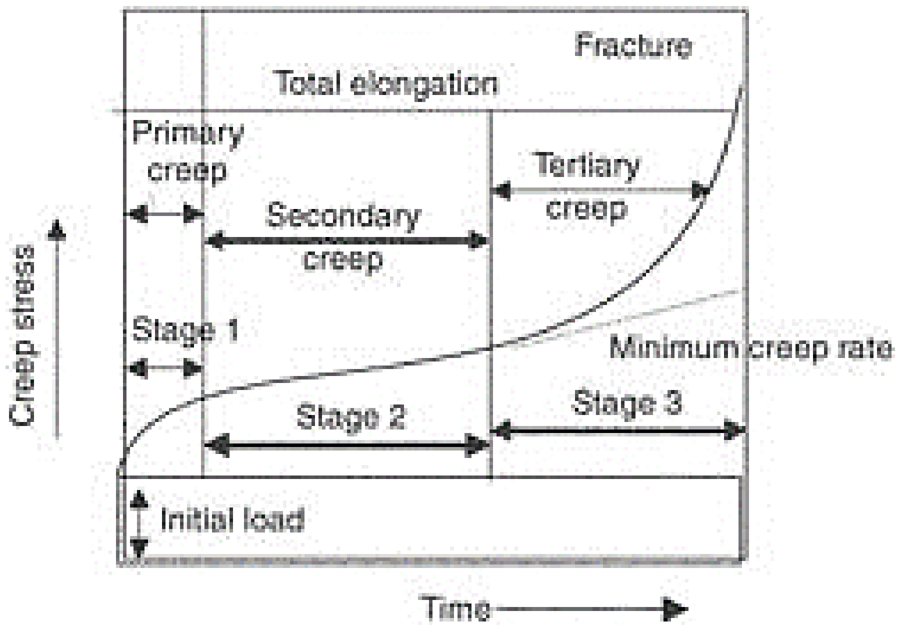
: Phenomenon which materials gradual are changed(are deformed) under a constant applied load(stress)
Normally, under a constant applied load at an elevated temperature ($T > 0.4\ T_m$)
→ **a time dependent dimensional change**
Jet engine (1% in 10,000 hrs), steam tube (1% in 100,000 hrs)

To determine the engineering creep curve of metal, a constant load is applied to a tensile specimen maintained at constant temperature and the strain of the specimen is determined as a function of time



Tensile test
: constant displacement determined stress

Creep test
: constant stress determined strain and time



- **Creep stages (3 steps)**

Primary creep (Transient)

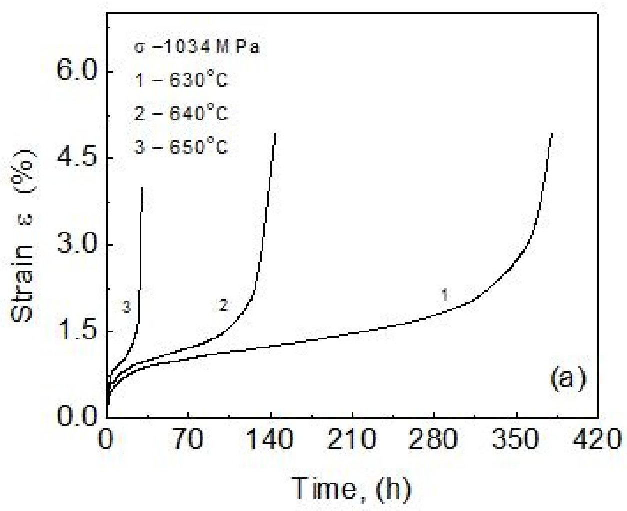
: strain rate decreases with increasing time → work hardening

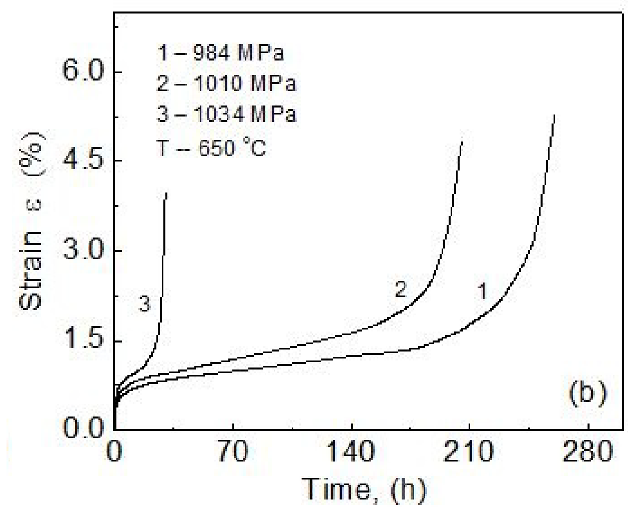
Secondary creep (Steady-state)

: balance between work hardening and recovery

Tertiary creep (Acceleration)

: strain rate increases due to creep damage (effective area decrease, metallurgical change)





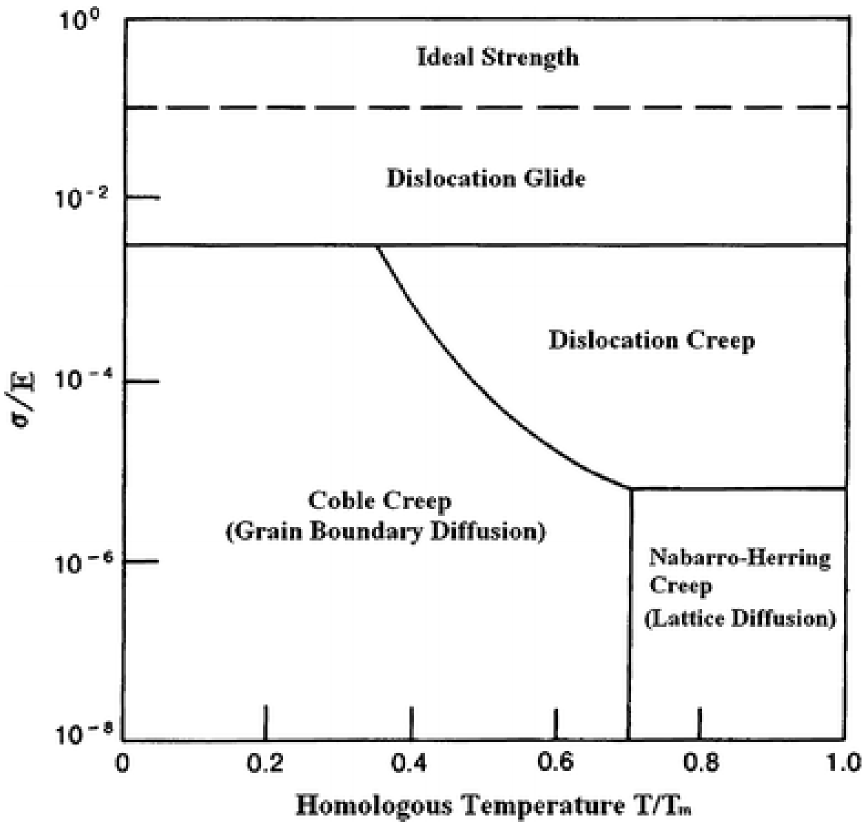
• Creep mechanisms

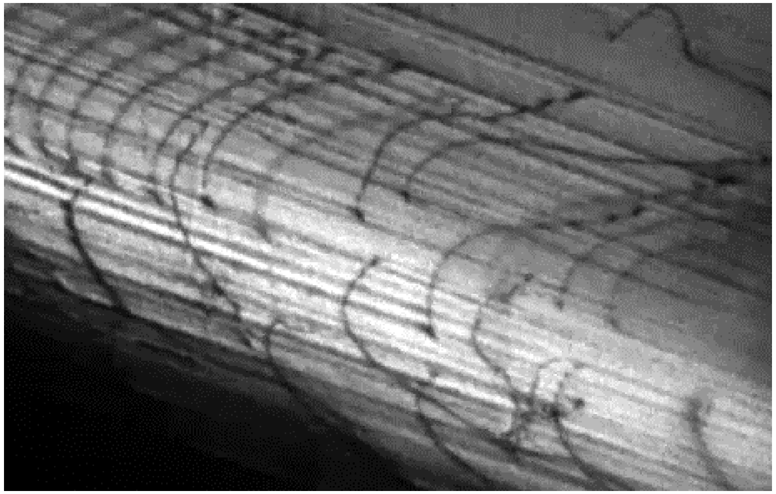
- Dislocation glide ($\sigma/G > 10^{-2}$)
Involves dislocation moving along slip planes and overcoming barriers by thermal activation
Occurs at high stress and low T

- Dislocation creep (climb, $10^{-1} > \sigma/G > 10^{-4}$)
Involves dislocation movement to overcome barriers by thermally assisted mechanisms involving diffusion of vacancies or interstitials

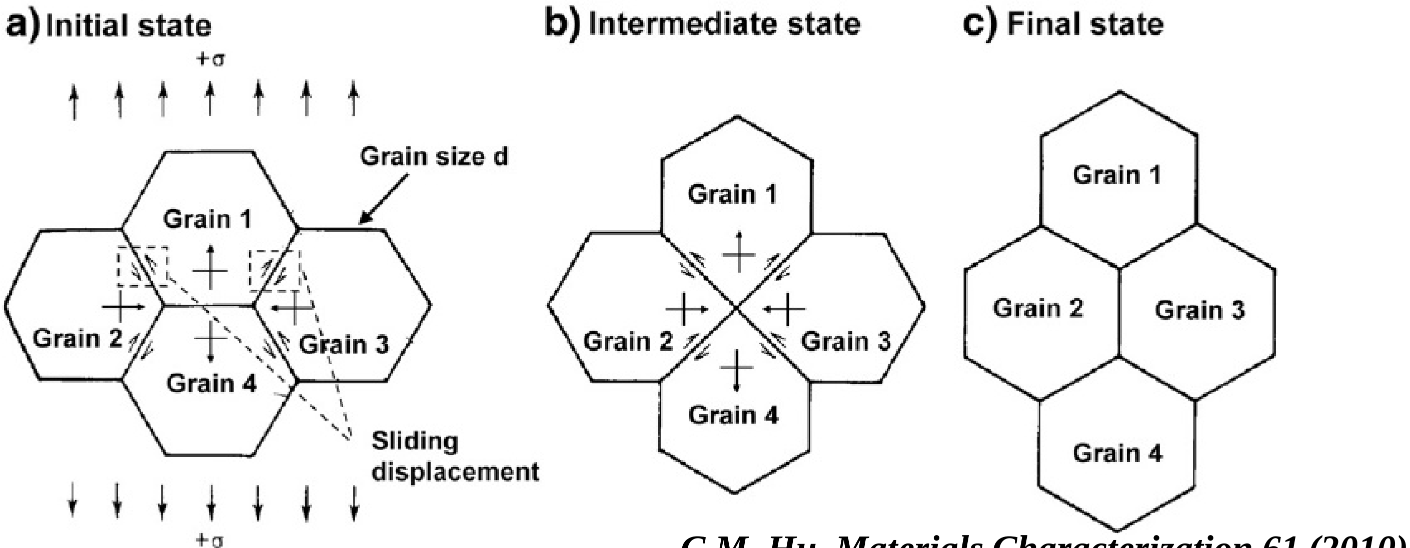
- Diffusion creep ($10^{-4} > \sigma/G$)
Involves the flow of vacancies and interstitials through a crystal under the influence of applied stress
Favored at high T and low stress
Bulk diffusion (Nabarro-Herring creep), GB diffusion (Coble creep)

- Grain boundary sliding
Involves the sliding of grains past each other





Josh Kacher, Acta Materialia 60 (2012) 6657–6672



C.M. Hu, Materials Characterization 61 (2010) 1043 – 1053

Strengthening mechanism

Solid Solution Hardening
Substitutional solid solution (Mo, W, Co..)
Interstitial solid solution (C, N, B)

Precipitation(Dispersion) Hardening
$\sigma = 0.8MGb/\lambda$

Work Hardening(Dislocation Hardening)
$\sigma_0 = \sigma_i + \alpha \mathrm{G} b \rho^{1/2}$

Grain Size Refinement Hardening
$\sigma_y = \sigma_0 + k\mathrm{D}^{-1/2}$

Secondary Phase Hardening
$\sigma_{ave} = f_1\sigma_1 + f_2\sigma_2$ f : volume fraction

But, Creep is time-dependent deformation
→ **Microstructure changes are effective**

Microstructural degradation → heterogeneous → failure

Carbo-Nitride

$M_{23}C_6$ ((Cr,Fe,Ni,Mo)$_{23}C_6$)

Crystal structure : FCC (a=10.57~10.68Å)

Precipitation site : Grain boundary, Twin boundary

Shape : Globular, Plate

Typical Size : 200~500nm

Initial stage : Precipitation hardening

Precipitate at grain boundary → depletion zone → Coarsening → Decreasing strength

MX precipitates (MC, MN, M(CN), M_1M_2(CN))

Alloy : Ti, Nb, V, Zr, Ta.. (strong carbide/nitride former)

Crystal structure : FCC (a=4.40~4.47Å)

Precipitation site : dislocation, stacking faults. Twin or grain boundary

Shape : Cuboidal shape after sufficient aging

Providing good strengthening effect

Stabilizing the alloy against intergranular corrosion

Z-Phase (CrNbN)

Crystal structure: Tetragonal (a=3.037Å, C=7.391Å)

Precipitation site : grain boundaries, twin boundary, dislocation

Shape : Rodlike, Cuboidal

Typical Size : 20~50nm

Z phase forms Nb stabilised steel with N at low temperature than MX particles.
Modified Z- phase : (Cr(Nb,V)N), CrVN
MX precipitates → Z-phase after long time annealing (stable phase below 1000°C)

M_2N (Cr_2N)

Crystal structure: Hexagonal close packed (a=4.78Å c=4.44Å)

Precipitation site : grain boundaries, twin boundary, dislocation

Shape : Rodlike, Cuboidal

Typical Size : 20~50nm

Intermetallic compound

Laves phase (Fe_2Mo, Fe_2Nb, Fe_2W, Fe_2Ta, Fe_2Ti)

Crystal structure : Hexagonal (a=4.73Å, C=7.72Å)

Precipitation site : Grain boundary,

Mo added steel : formation after a minimum of 1000h between 625~800^{o}C

Nb stabilized steel : after long time aging, 5000~10000h between 625~800^{o}C

→ However, NbC and Z phase are more stable than Laves phase

σ-Phase $(Fe,Ni)_x(Cr,Mo)_y$

Crystal structure : Tetragonal (a=8.80Å, C=4.54Å)

Precipitation site : Grain boundary, Twin boundary, Inclusion

The precipitates form after long term aging at high temperature (10,000~15,000h, 600^{o}C)

G Phase ($Ni_{16}Nb_6Si$, $Ni_{16}Ti_6Si_7$, $(Ni,Fe,Cr)_{16}(Nb,Ti)_6Si_7$) (austenitic stainless steel)

Crystal structure : FCC Phase (a=1.115~1.12Å)

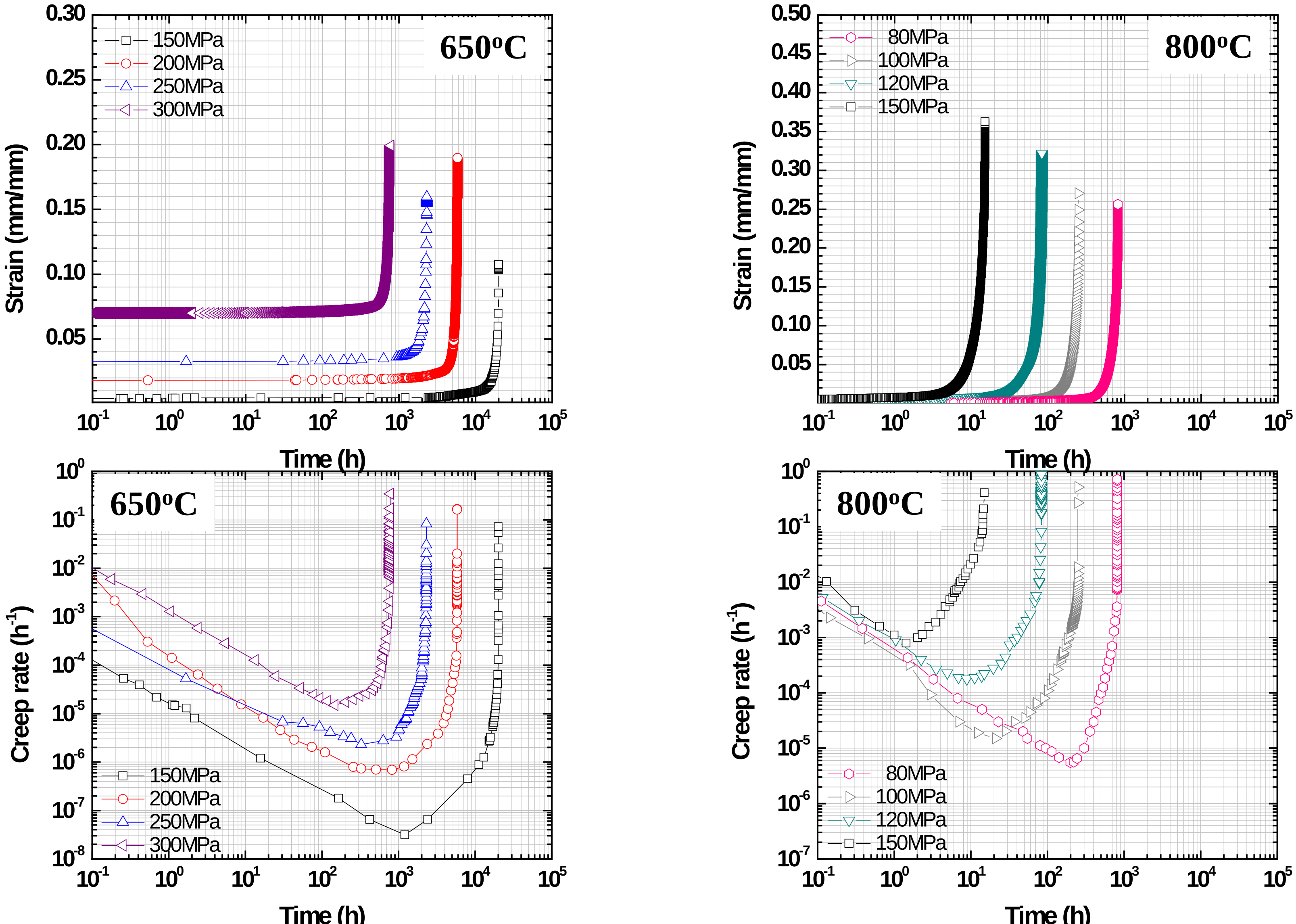
Table 6 Crystal structures and compositions of main precipitates in austenitic stainless steels

Precipitate	Structure	Parameters, nm	Composition
NbC	fcc	a=0·447	NbC
NbN	fcc	a=0·440	NbN
TiC	fcc	a=0·433	TiC
TiN	fcc	a=0·424	TiN
Z phase	tetragonal	a=0·3037, c=0·7391	CrNbN
$M_{23}C_6$	fcc	a=1·057–1·068	$Cr_{16}Fe_5Mo_2C_6$ (e.g.)
M_6C	diamond cubic	a=1·062–1·128	$(FeCr)_{21}Mo_3C$, Fe_3Nb_3C, M_5SiC
σ phase	tetragonal	a=0·880, c=0·454	Fe–Ni–Cr–Mo
Laves phase	hexagonal	a=0·473, c=0·772	Fe_2Mo, Fe_2Nb
χ phase	bcc	a=0·8807–0·8878	$Fe_{36}Cr_{12}Mo_{10}$
G phase	fcc	a=1·12	$Ni_{16}Nb_6Si_7$, $Ni_{16}Ti_6Si_7$

T. Sourmail, Precipitation in creep resistant austenitic stainless steels, Materials Science and Technology, 17 (2001) 1-14

Typical creep curve

D-B Park, PhD thesis, Korea univ (2013)



Stress dependences of minimum creep rates

Norton law (Power law)

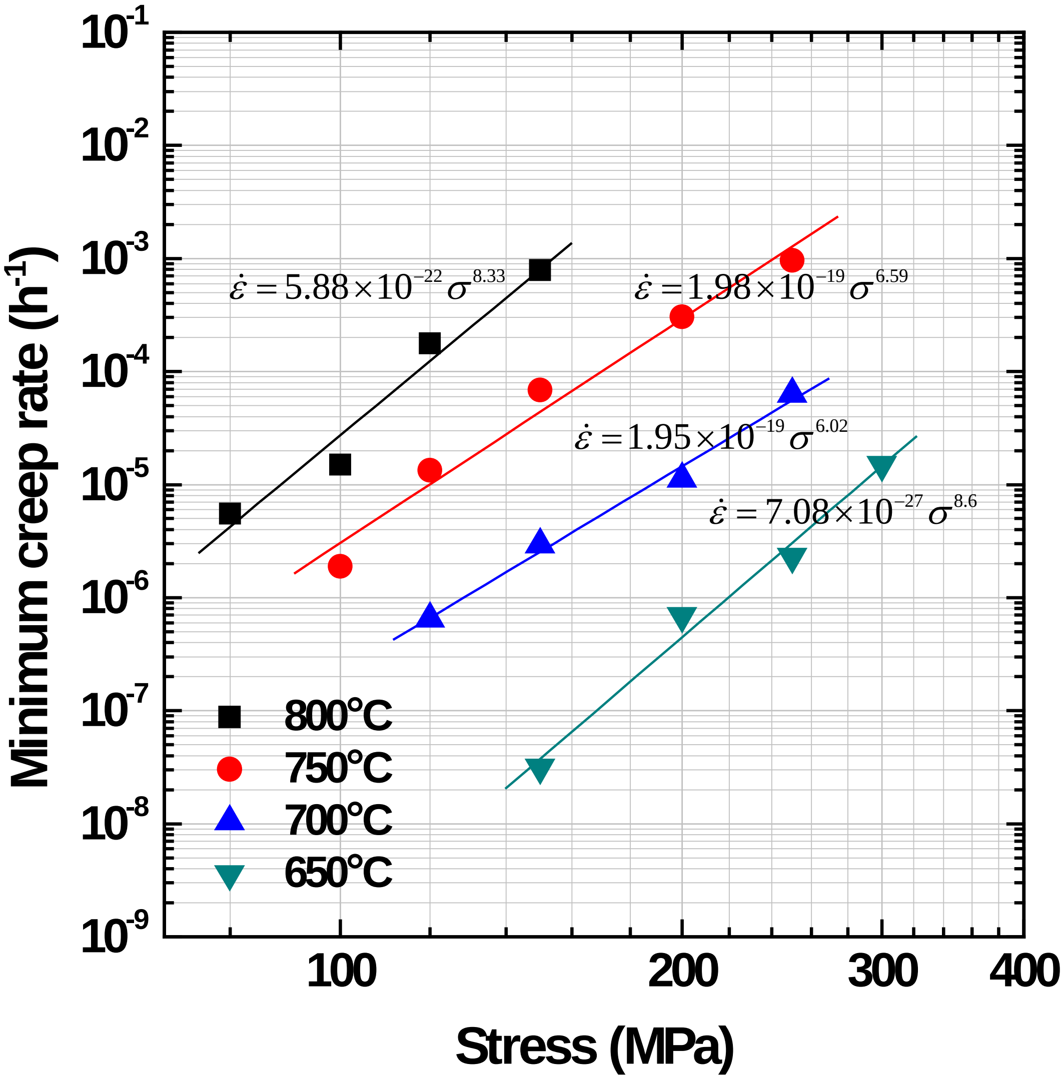
$$\dot{\varepsilon}_m = A\sigma^n$$

Dislocation creep

n=3~5
: pure metal, simple alloy

n=3~12
austenitic stainless steel

In this study
n=6~8.6

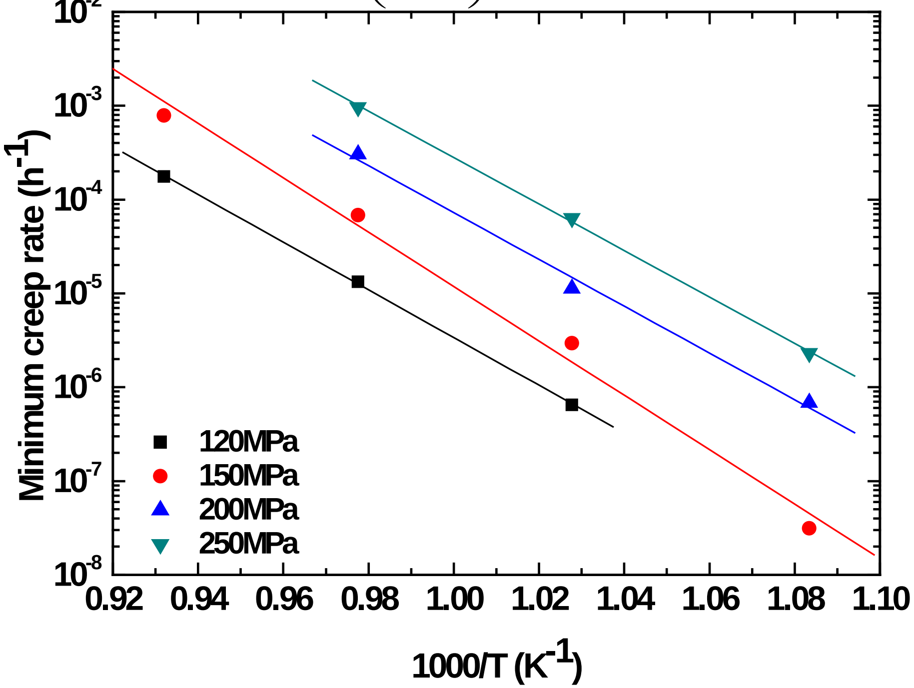


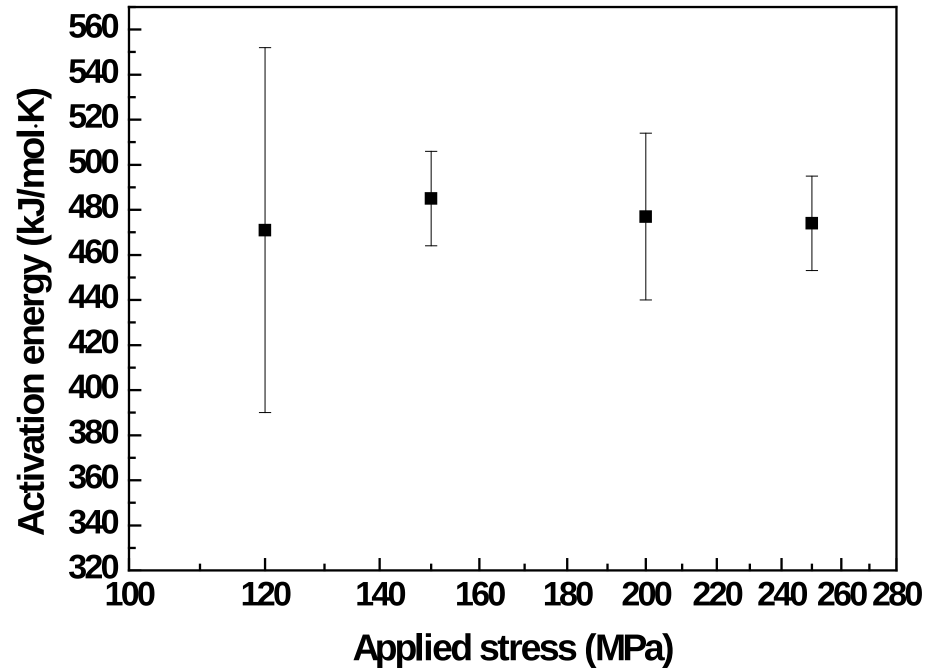
Dae-Bum Park, Materials Characterization 93 (2014) 52 – 61

Dae-Bum Park, Materials Characterization 93 (2014) 52 – 61

Activation energy for dislocation creep

$$\dot{\varepsilon} = A\sigma^{n} \exp\left(\frac{-Q}{RT}\right)$$





γ-Fe self diffusion activation energy : 295kJ/mol
14Cr-15Ni-Ti austenitic stainless : 460kJ/mol
347H austenitic stainless steel : 441~461kJ/mol
TP347H austenitic stainless steel : 385~463kJ/mol

The similarly value of apparent activation energy (465~485kJ/mol)

Kyu-Ho Lee, Materials Characterization 102 (2015) 79–84

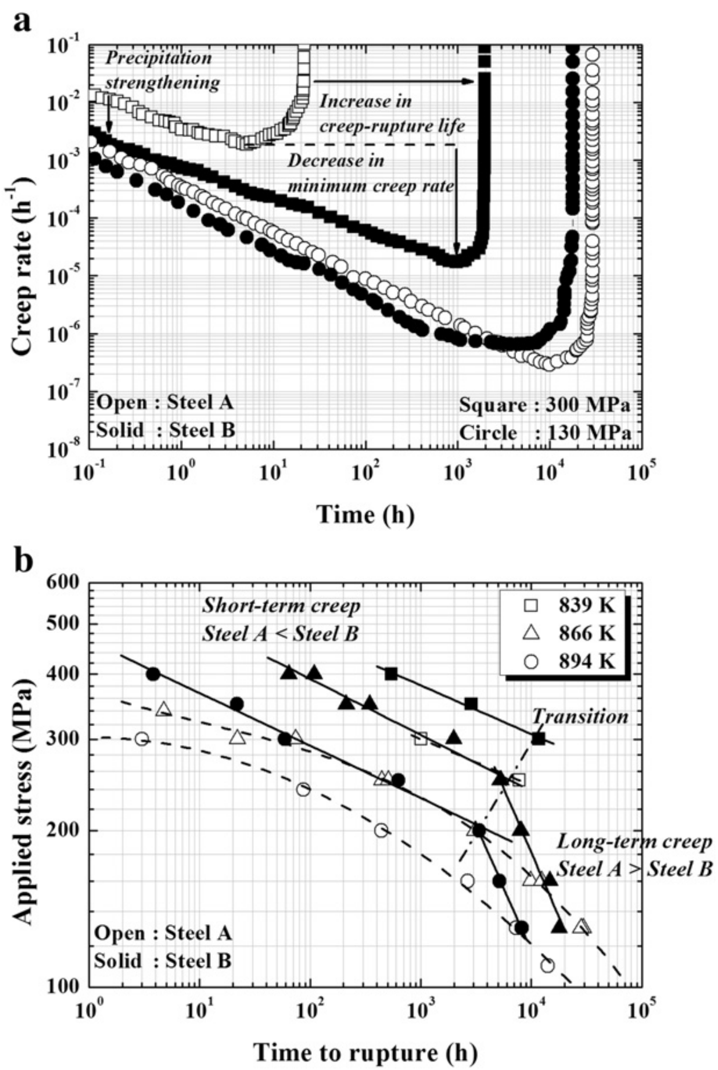


Fig. 4. (a) Creep rate versus time tested at 866 K and (b) creep-rupture plot of the Steel Aand Steel B acquired at various creep conditions.

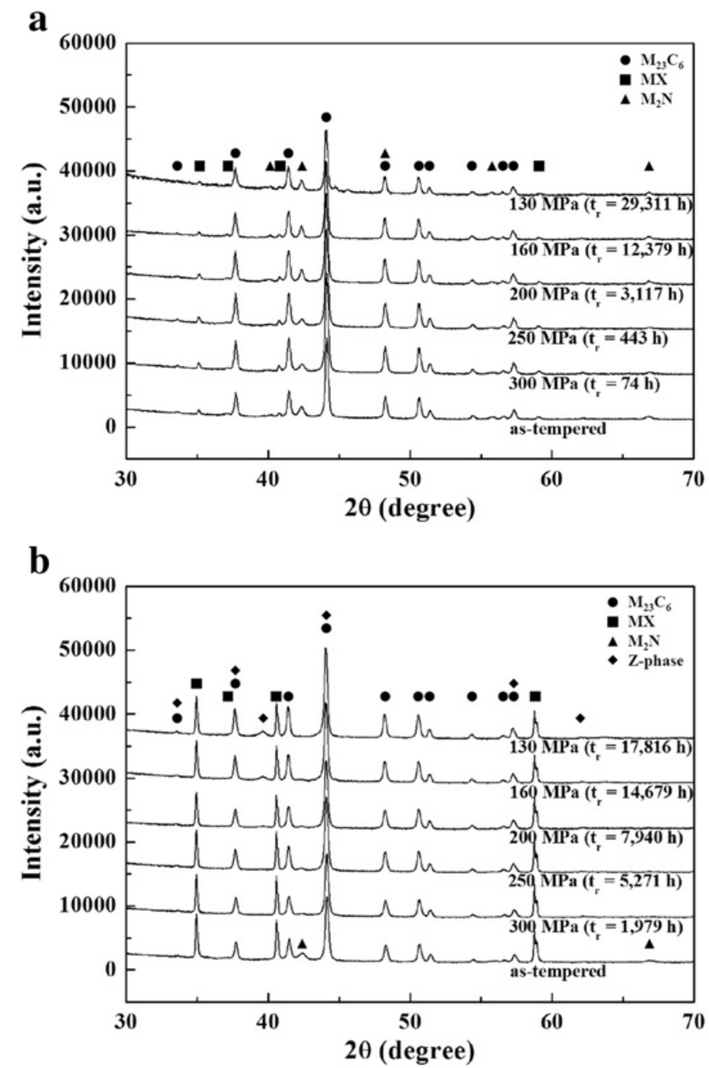


Fig. 5. XRD profiles of the powders electrolytically extracted from the gauge part of creep specimens of (a) Steel A and (b) Steel B tested at 866 K.

Kyu-Ho Lee, Materials Characterization 102 (2015) 79–84

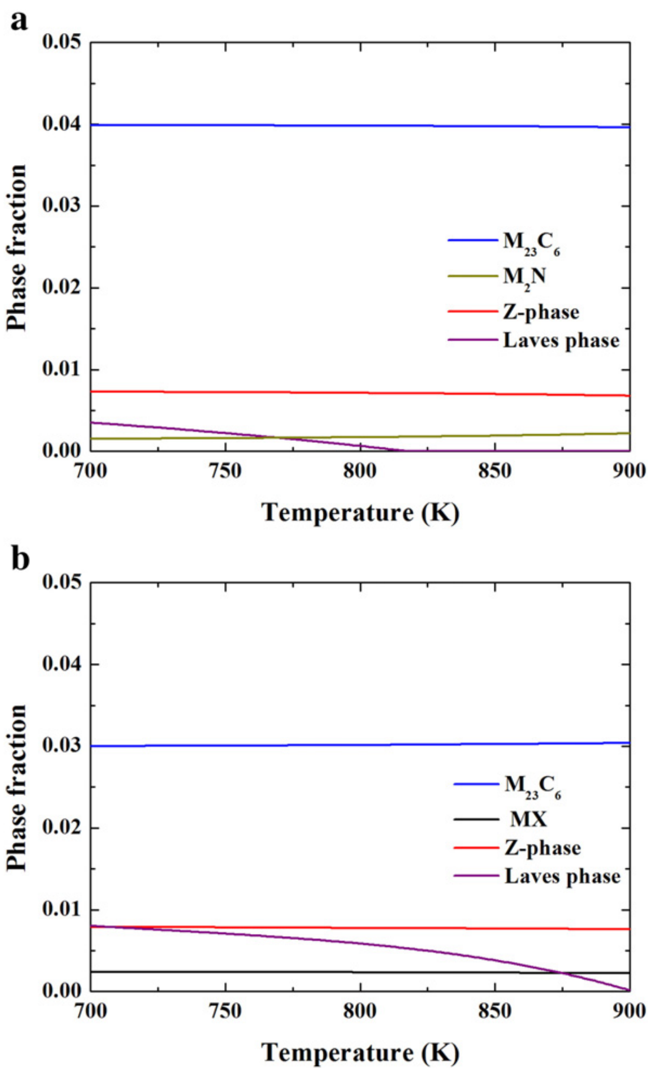


Fig. 7. Equilibrium phase fraction of high-Cr martensitic heat-resistant steels, (a) Steel A and (b) Steel B calculated by MatCalc.

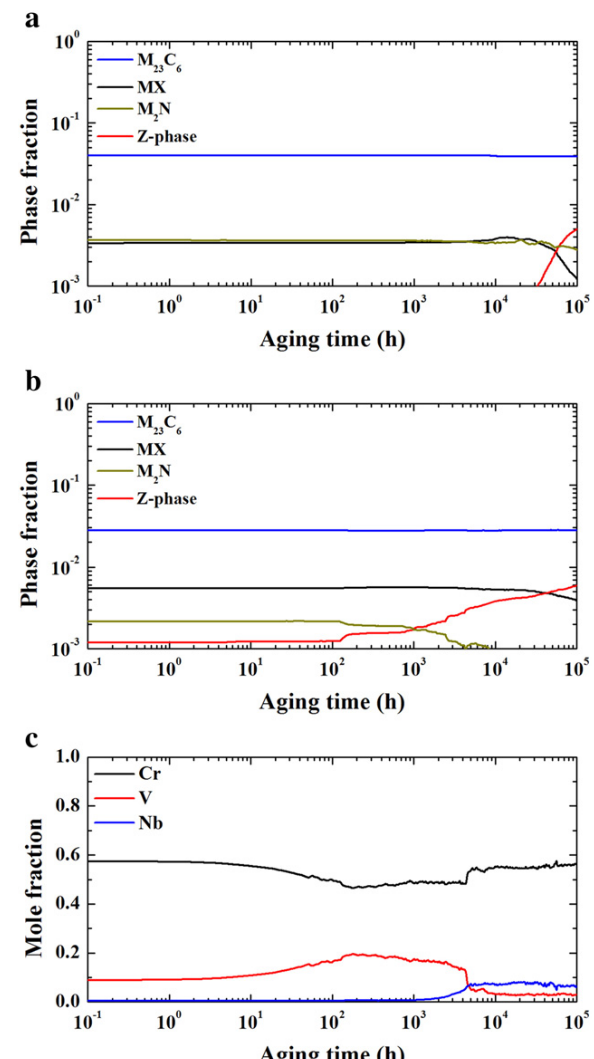
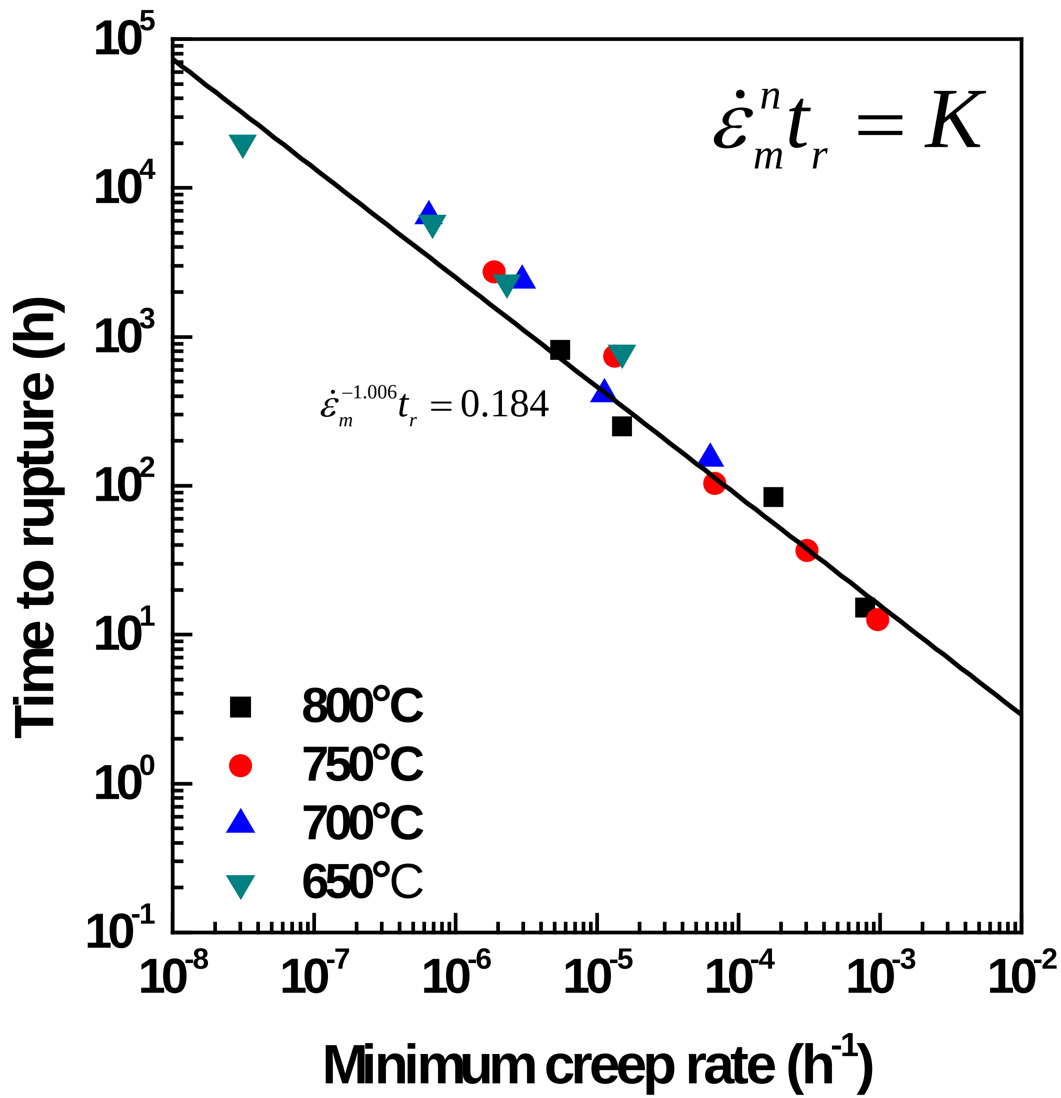
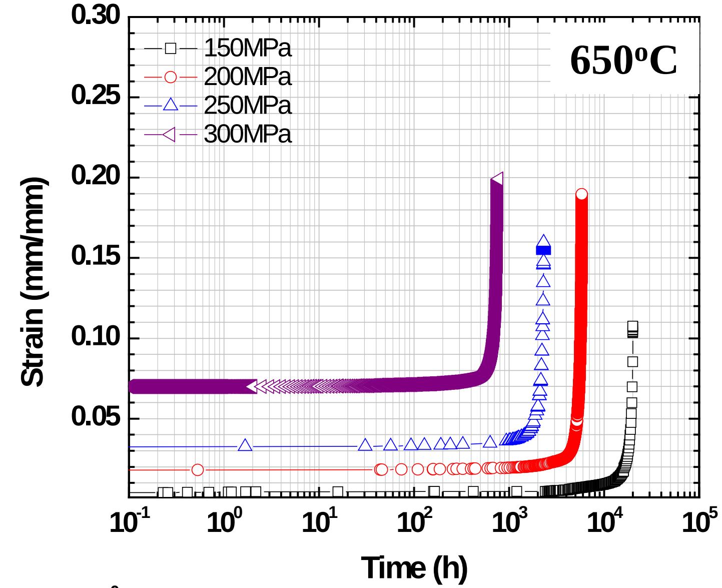
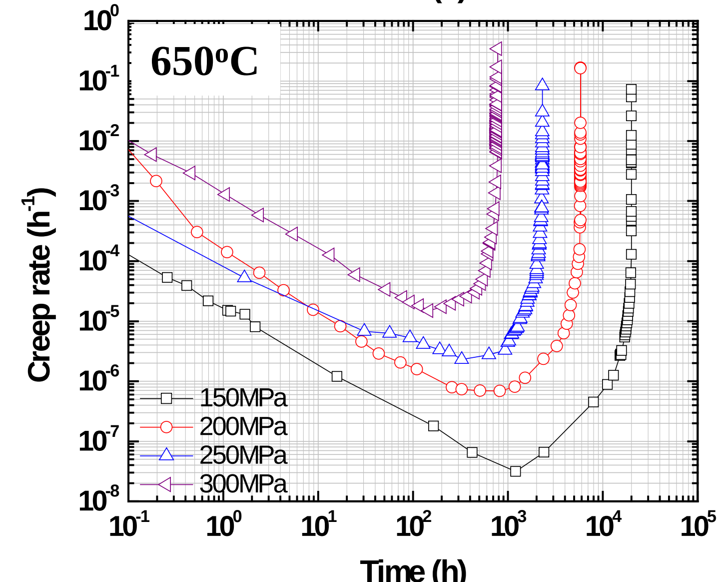


Fig. 8. Development of phase fraction of the precipitates in (a) Steel A, (b) Steel B and (c) chemical composition ofM2N in Steel B during aging at 866 K calculated by thermo-kinetic simulation.

Monkman-Grant relationship (predict the rupture time)



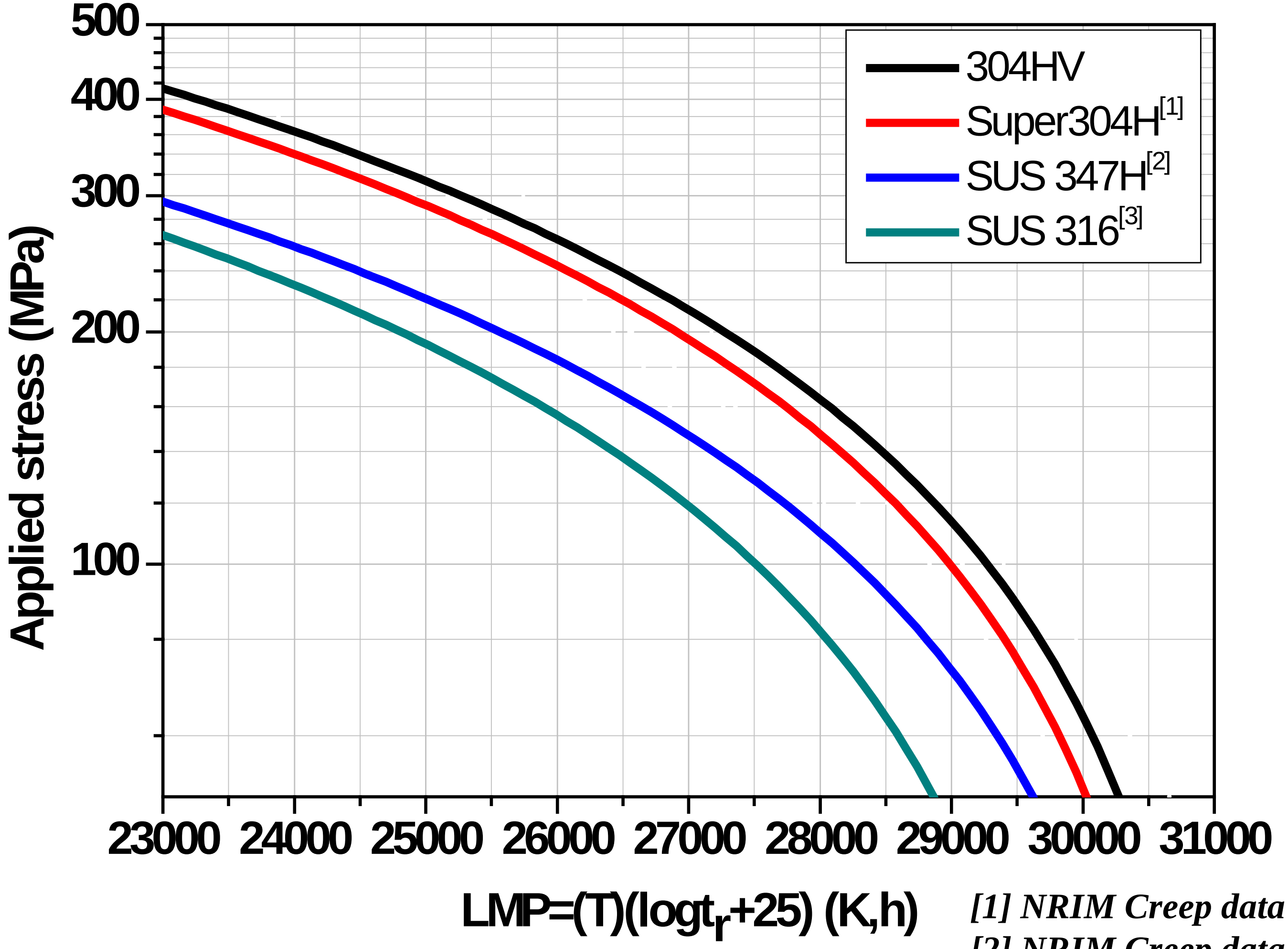




Dae-Bum Park, Materials Characterization 93 (2014) 52 – 61

Larson-Miller plot (predict the rupture time)

$$T(\log t_r + C) = K$$



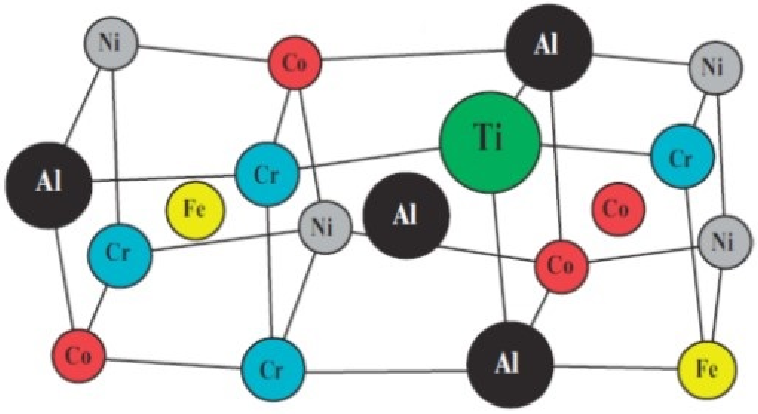
[1] NRIM Creep data sheep No. 56
[2] NRIM Creep data sheep No. 28B
[3] NRIM Creep data sheep No. 6B

Dae-Bum Park, Materials Characterization 93 (2014) 52 – 61

❖High Entropy alloy(HEA) Introduction

Definition

: At least five major metallic element having an 5-35 at%



➢ **Core effect**

1) Solid solution strengthening
2) Distorted lattice structure
3) Cocktail effect
4) Sluggish effect

5) Nanoscale deformation twin (Cantor alloy)

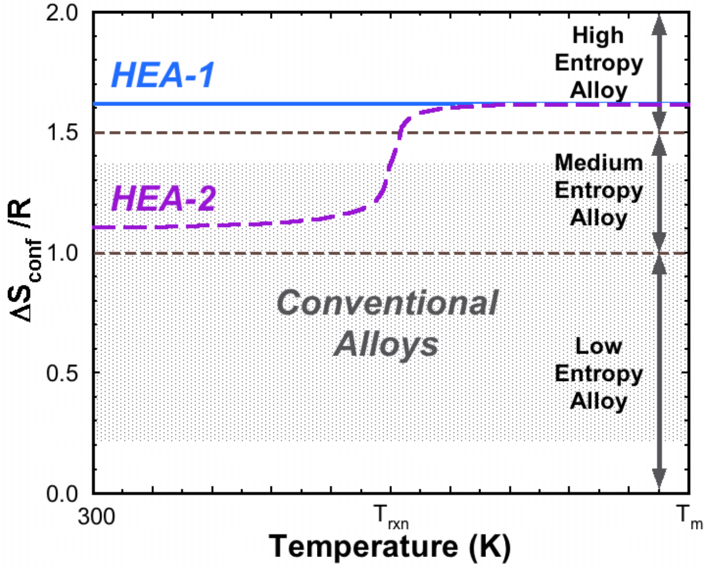
B. Cantor, Materials Science and Engineering A 375–377 (2004) 213–218

→ FeCrMnNiCo

Yeh, Advanced Engineering Materials, 6, 5 (2004) 299-303

→ High-Entropy alloys (HEAs)

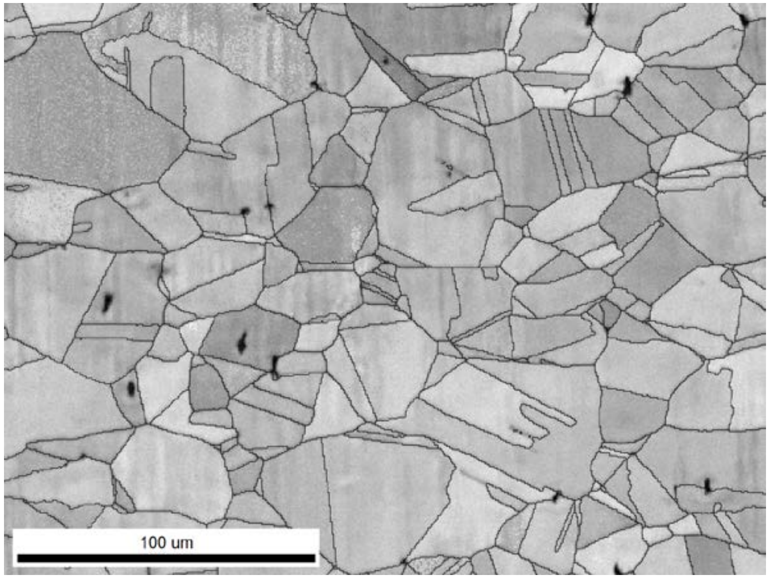
$$\Delta S_{conf} = -R\sum_{i=1}^{N} n_i \ln n_i$$



Daniel B. Miracle, "Exploration and Development of High Entropy Alloys for Structural Applications", Entropy (2014), 16, 494-525

Initial specimen information

- EBSD IQ(Microstructure)

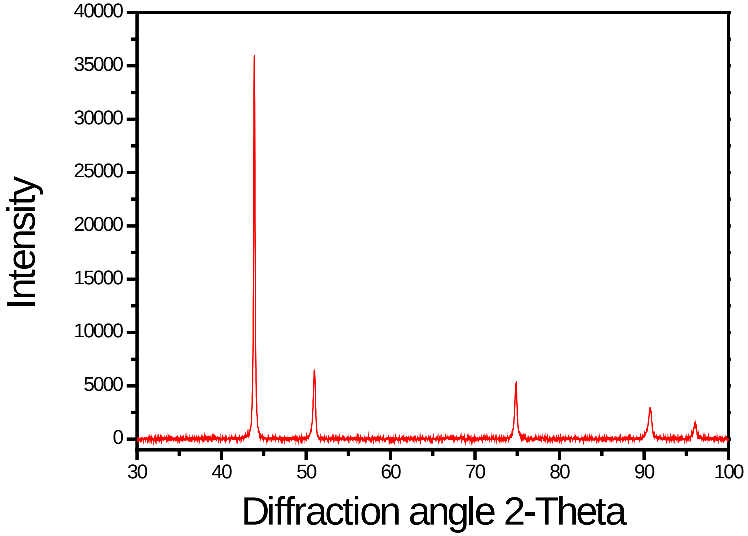


50.34μm±19.89

- EDS

Element	Wt%	At%
CrK	18.30	19.76
MnK	18.36	18.75
FeK	19.95	20.80
CoK	21.18	20.92
NiK	19.94	19.78
Matrix	Correction	ZAF

- XRD



FCC singe phase

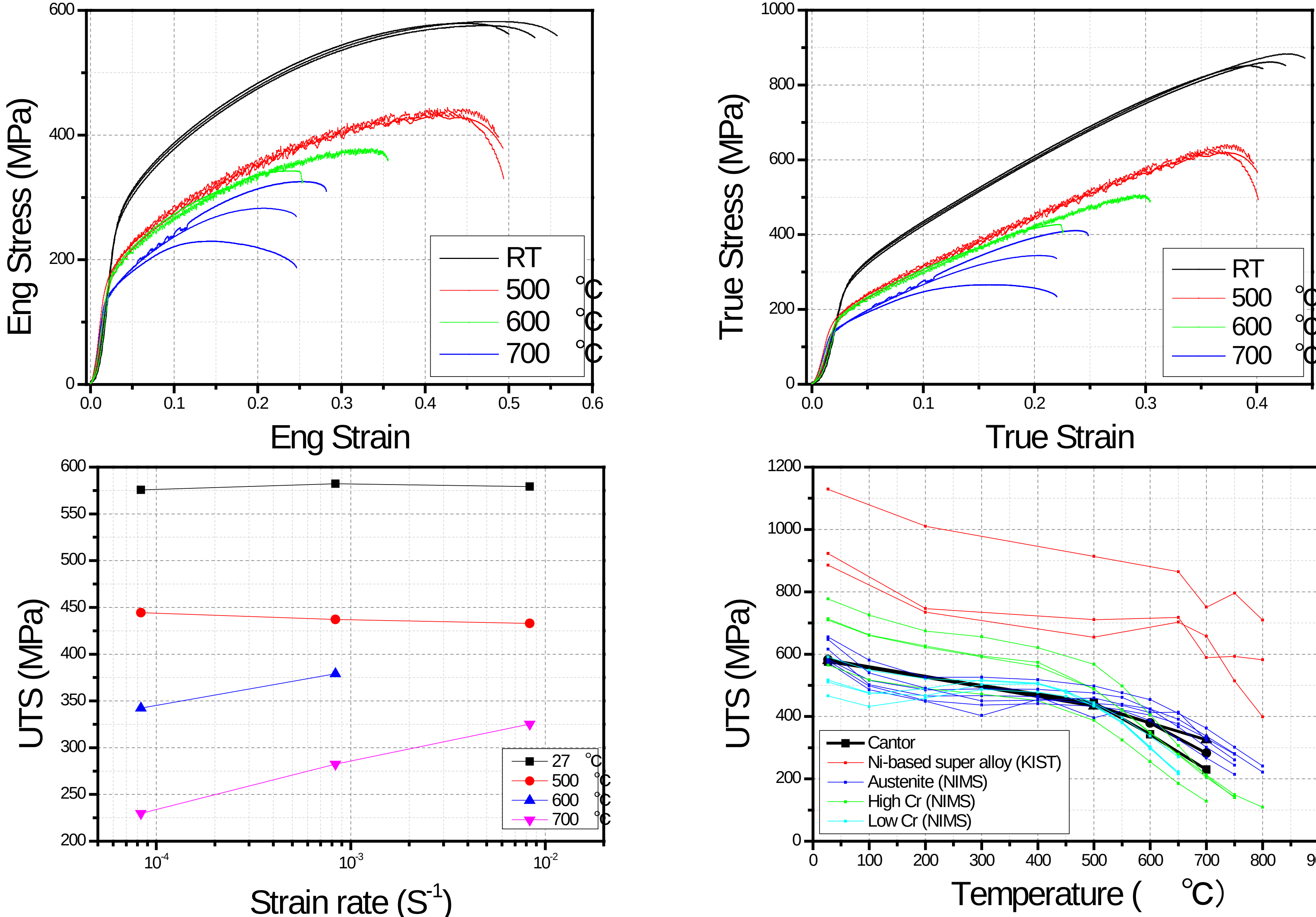
Lattice parameter* : 3.58238 Å

(*:Bragg's law와 d-spacing으로 얻은 각각의 면들의 lattice parameter의 평균)

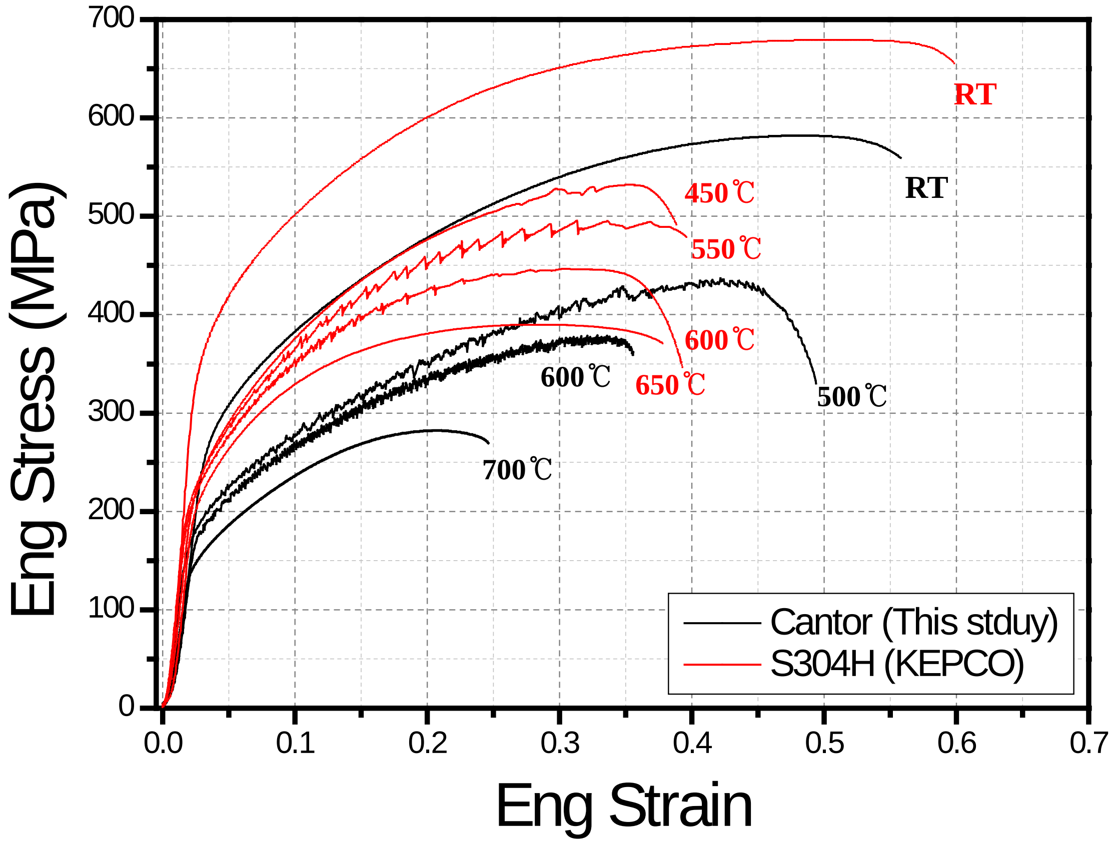
- Vickers hardness

161Hv±2.677

Tensile results



Tensile results compared with S304H

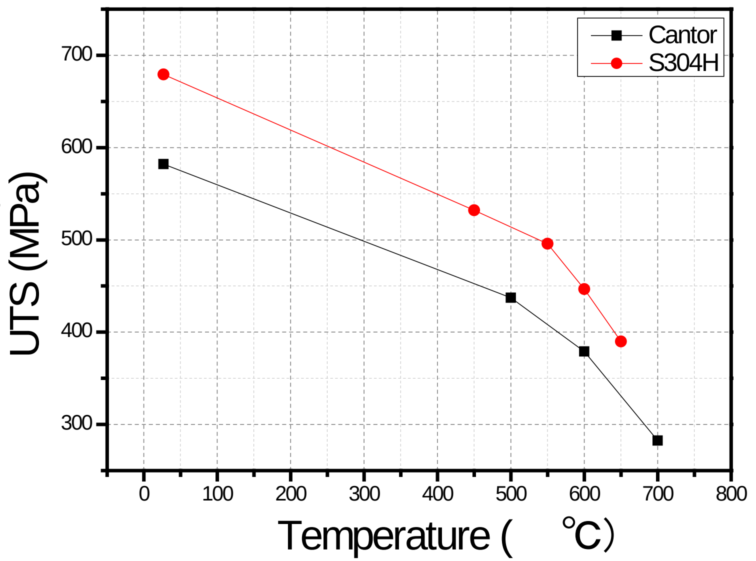


- Cantor

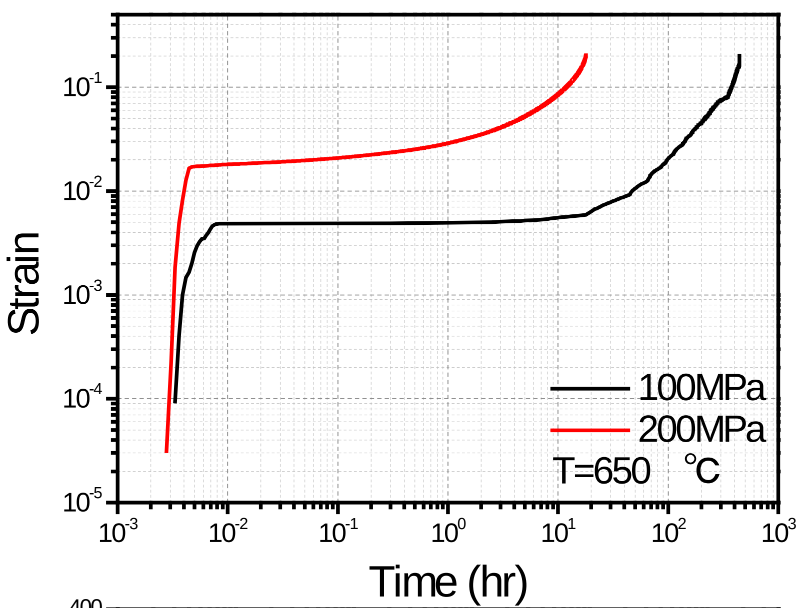
Strain rate : 8.333x10^{-4}

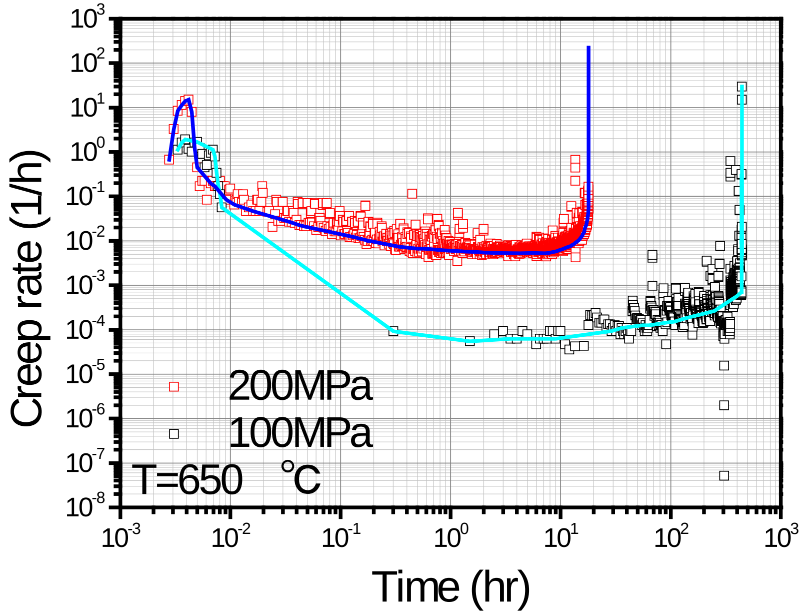
- S304H

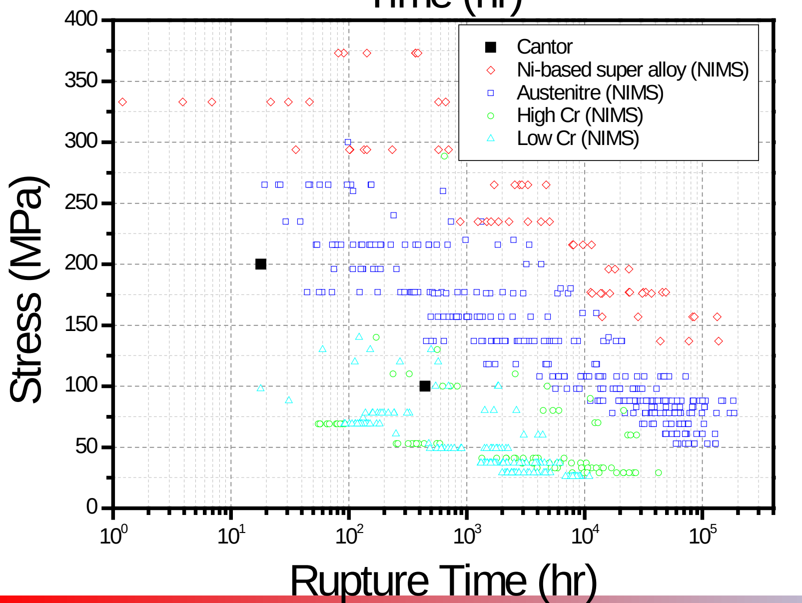
Strain rate : 6.666x10^{-4}



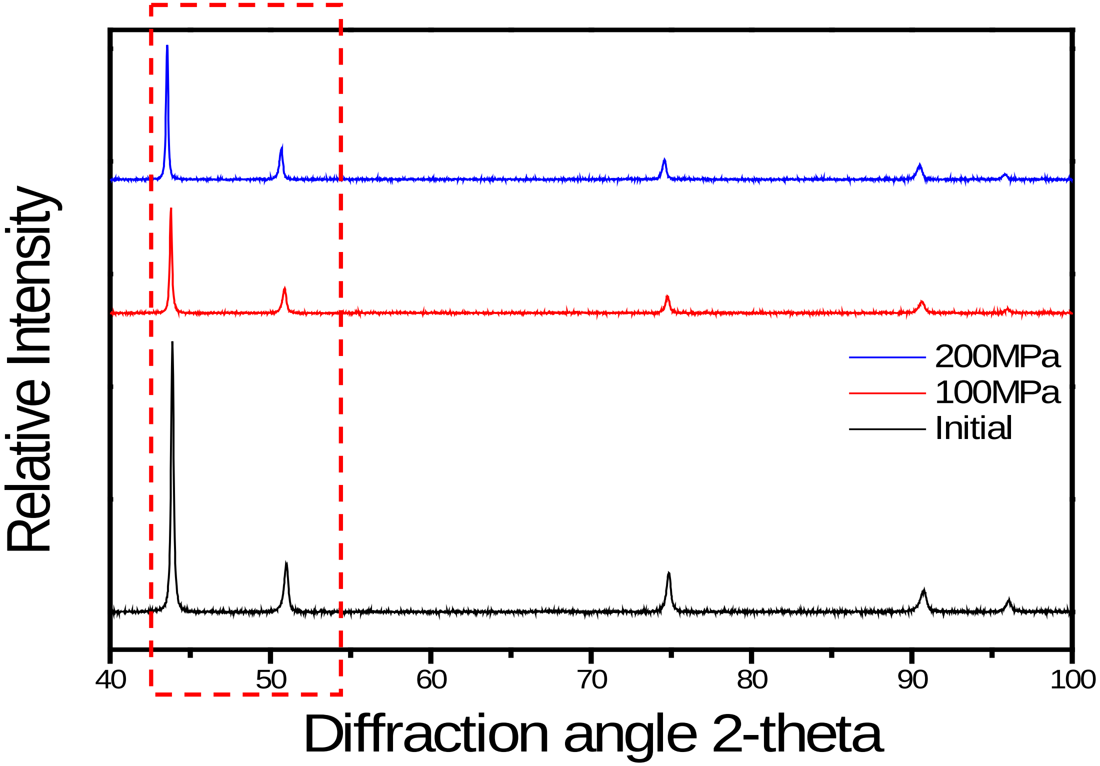
Creep results





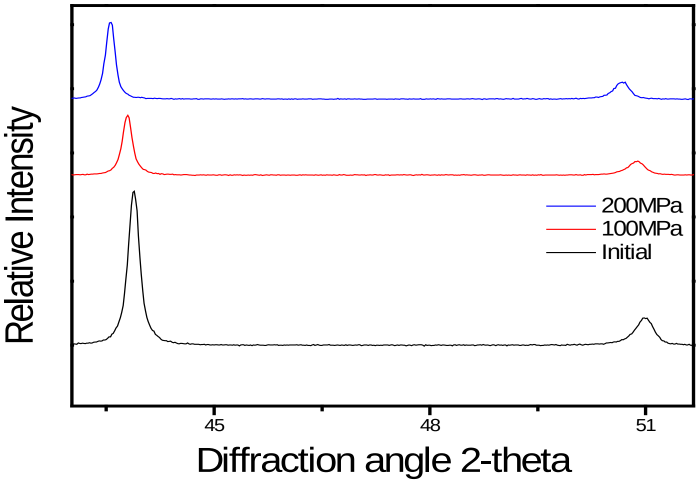


XRD results after creep test



Specimen	Initial	100MPa	200MPa
Crystal structure	FCC	FCC	FCC
Lattice parameter*(Å)	3.58238	3.58729	3.59578

(*:Bragg's law와 d-spacing으로 얻은 각각의 면들의 lattice parameter의 평균)



Summary

- To improve efficiency of coal thermal power station, increase of operating temperature is required. Therefore, research on heat-resistant material should be preceded.

- Materials with high heat-resistance, oxidation-resistance, corrosion-resistance, weldability and especially creep-resistance are required as the structural materials for the thermal power station application.

- Creep phenomenon is a time-dependent deformation behavior and microstructural change is dominant effect on the failure of materials.

- Through the creep test condition under high temperature and constant load compare to the real operating condition, we expect to predict the lifetime of structural materials for the thermal power station.

Thank you for your attention