EUROMAT 2005

Assessment of High Chromium Oxide Dispersion Strengthened Steels for Nuclear Applications

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J.S. Lee[1], I.S. Kim[2], C.H. Jang[2], A. Kimura[3]
jslee2@kaist.ac.kr
1) Center for Advanced Reactor Research, KAIST, Daejeon, Republic of Korea
2) Department of Nuclear and Quantum Engineering, KAIST, Daejeon, Republic of Korea
3) Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Japan

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- Summary

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Introduction

- Oxide dispersion strengthening (ODS) steels

  - Candidate material for fusion reactor blanket, fuel clad in FBR, and high burn-up LWR

  Requirements for fuel clad application

  - high resistance to irradiation embrittlement and swelling
  - corrosion resistance in high temperature water environment
  - low susceptibility to hydrogen-induced cracking and SCC
  - lower DBTT shift by thermal aging embrittlement

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Corrosion properties

- Strong corrosion resistance in SCWR

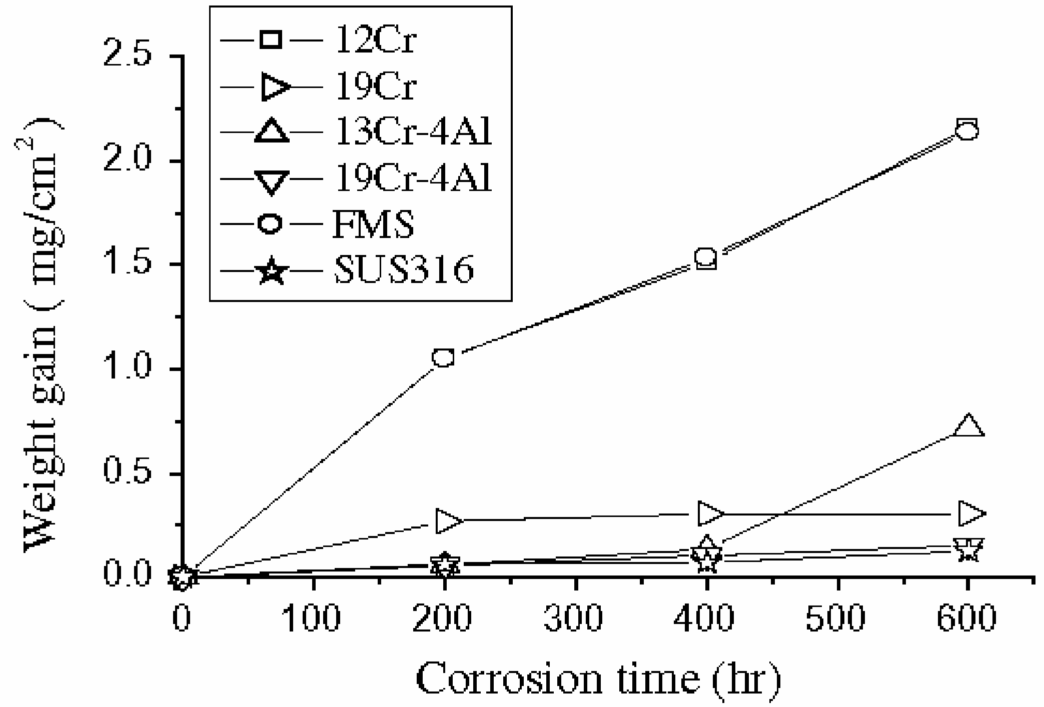

Fig. 2. The effect of Cr and Al on the corrosion properties of ODS ferritic/martensitic steel in SCPW (783 K, 25 MPa).

H.S. Cho, A. Kimura, S. Ukai, M.Fujiwara, *J. Nucl. Mater.* 329-333 (2004) 387-391.

- General hydrogen and thermal aging effects in a high Cr steel

  - reduction in ductility and toughness

  - brittle fracture (intergrannular or transgrannular)

- Objectives

  - to investigate the *effects of hydrogen and thermal aging on the mechanical properties* of ODS steels d epending on the anisotropy of deformation structure

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Experimental

- Test materials

  -K1; 18.37Cr-0.29W-0.28Ti-0.368Y_2O_3

  -K2; 13.64Cr-1.65W-4.12Al-0.28Ti-0.381Y_2O_3

  -K3; 16Cr-1.82W-4.59Al-0.28Ti-0.368Y_2O_3

  -K4; 18.85Cr-1.83W-0.28Ti-4.61Al-0.368Y_2O_3

  -K5; 22.05Cr-1.8W-4.55Al-0.27Ti-0.356Y_2O_3

  -RMS; 9Cr-2W-0.03Al

Fe-xCr-yW-zAl / Argon gas atomized powder

Y_2O_3, Ti Powders

Mechanically alloyed by ball mill

Canning and degassing

Hot extrusion

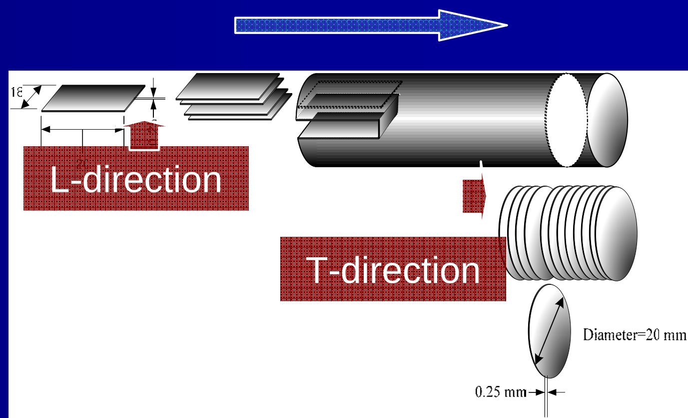
(1423 K, 67 mm dia. to 25 mm dia.)

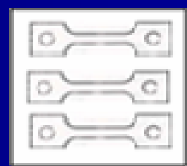
Heat treatment

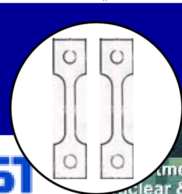
(1423K x 1h+ air cooling)

Machining

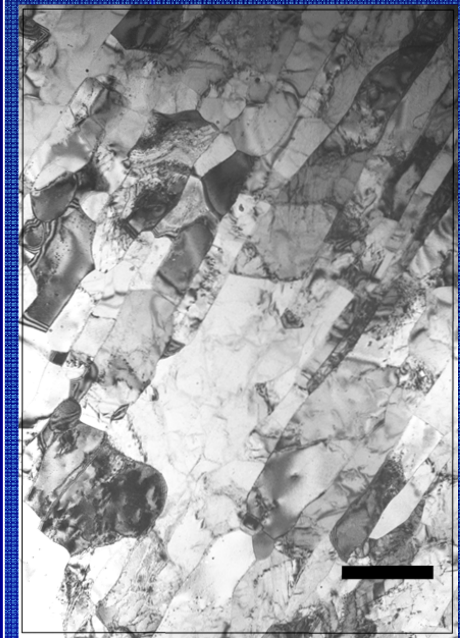
Extrusion direction



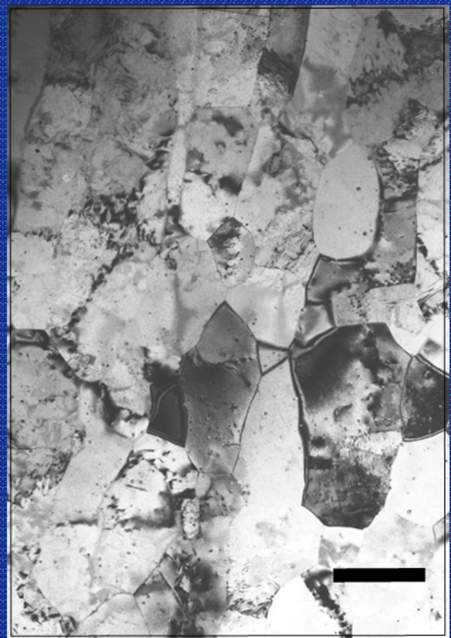




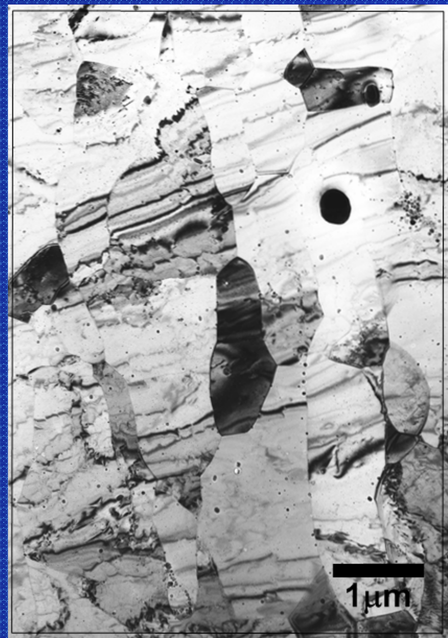
Microstructural characteristics of ODS Steels



K1 ODS



K2 ODS



K4 ODS

K5 ODS

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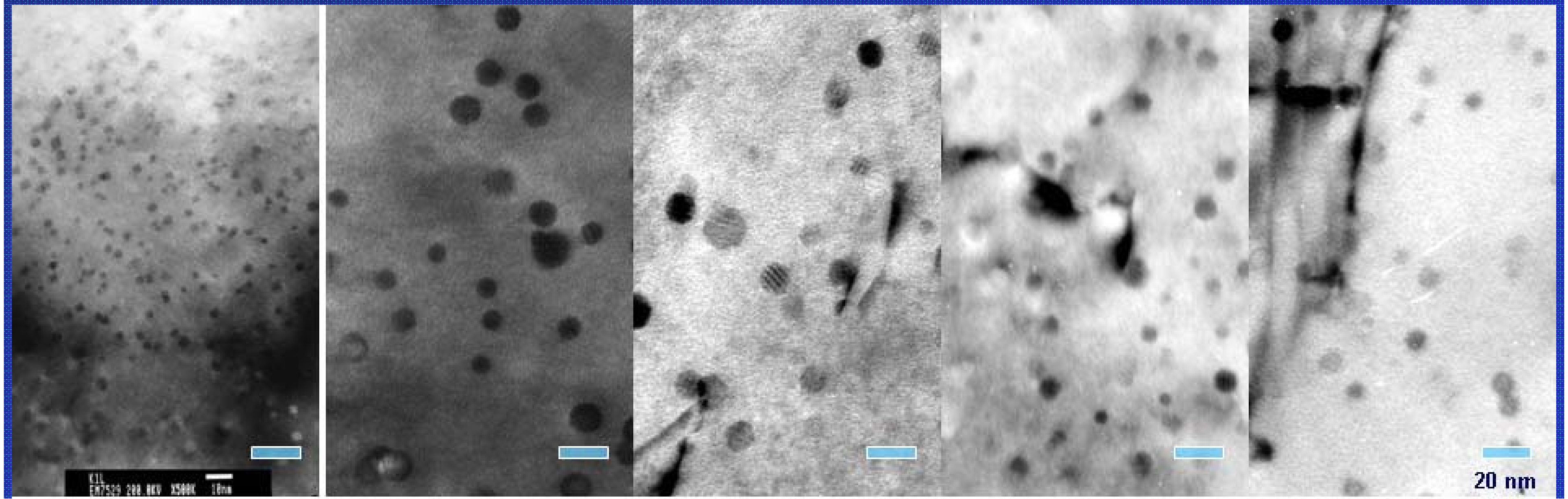
Size & number density of oxide particles

K1 ODS	K2	K3	K4	K5



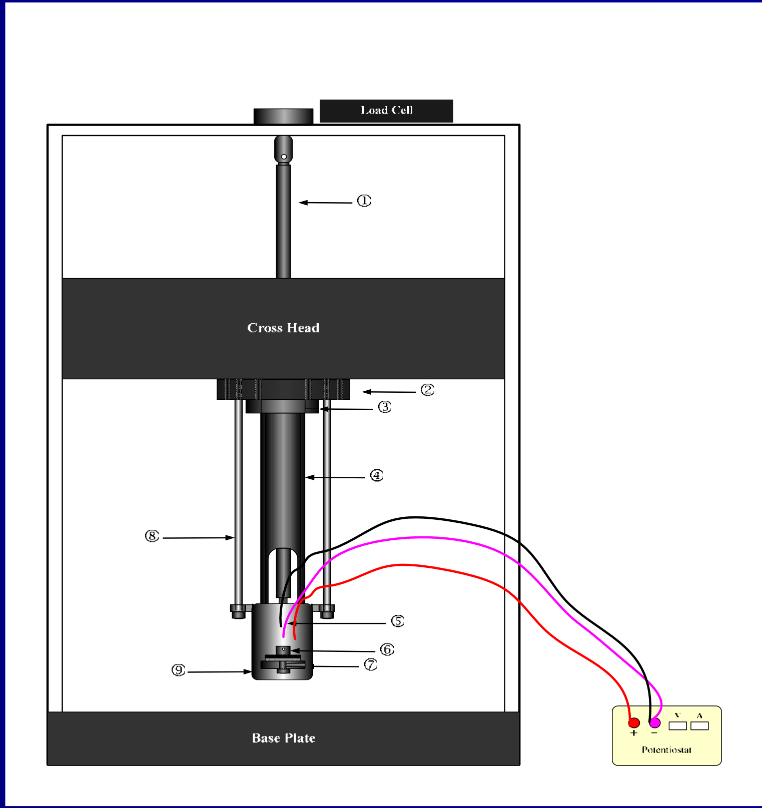
	Size (nm)	Density (m^{-3})	Average spacing (nm)
K1 (19Cr)	2.4	1.4×10^{23}	65
K2 (13Cr-4Al)	6.3	2.3×10^{22}	95
K3 (16Cr-4Al)	6.8	1.4×10^{22}	118
K4 (19Cr-4Al)	6.7	1.6×10^{22}	112
K5 (22Cr-4Al)	7.3	1.3×10^{22}	118

Hydrogen Effects

Hydrogen charging during tensile test

- Hydrogen charging conditions
  - cathodic charging
  - solution; 1N H_2SO_4 + 10 mg/l As_2O_3
  - pre- (30 min.) + *in-situ* charging
  - current density; 100 ~ -520 A/m^2
- Test Temperature
  - 297 K
- Strain rate
  - 9x10^{-5} /s
- Hydrogen contents
  - measured by TDS

Tensile Testing system



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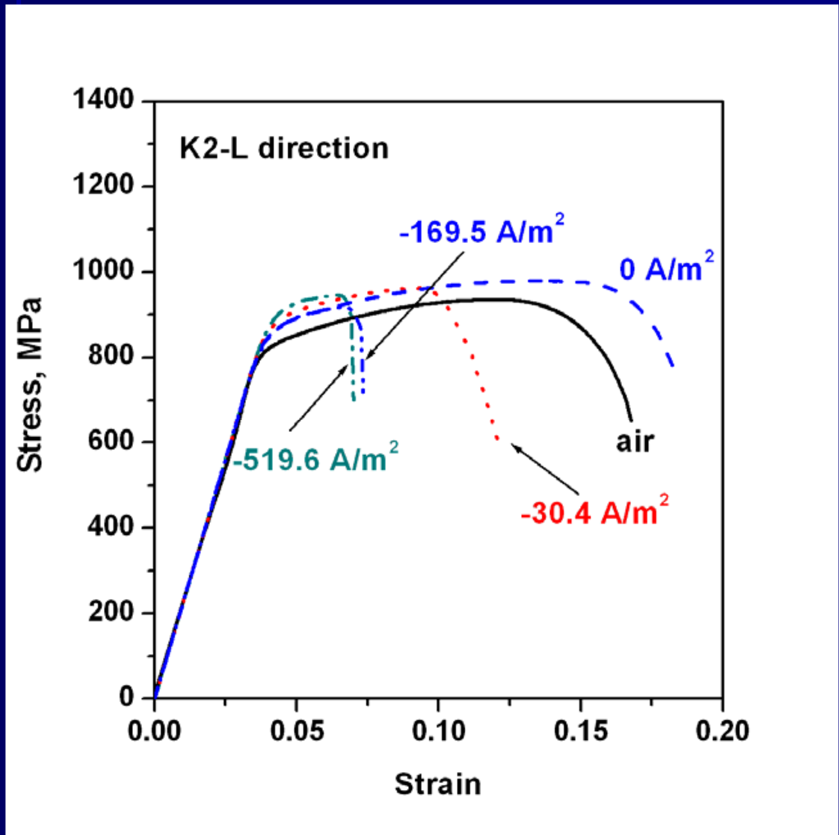
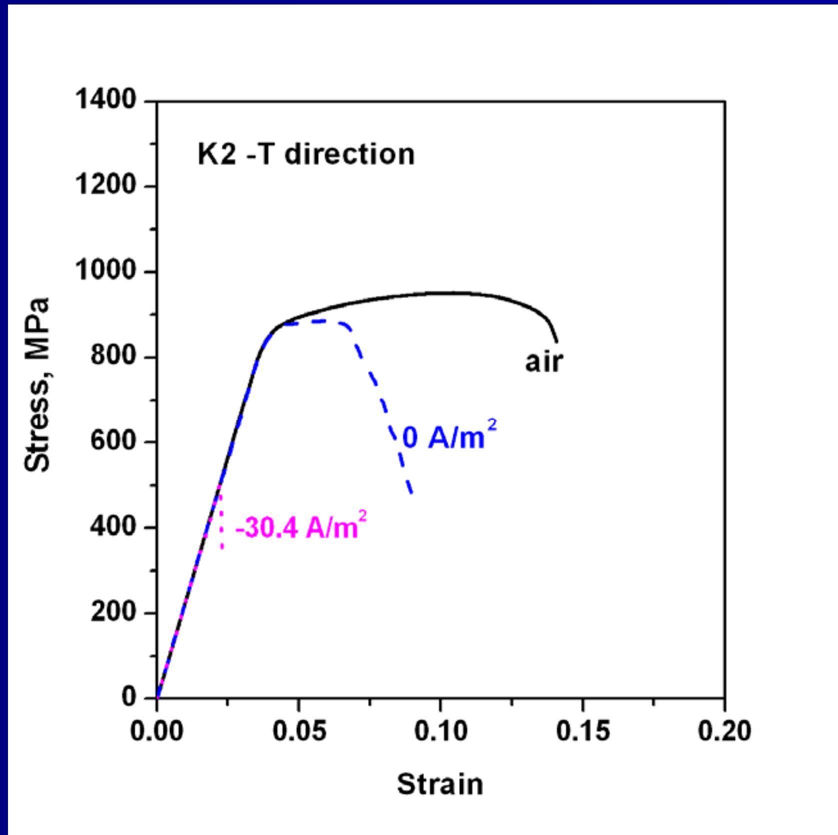
Tensile stress-strain curves

K2 ODS (13Cr-4Al)

L-direction



T-direction



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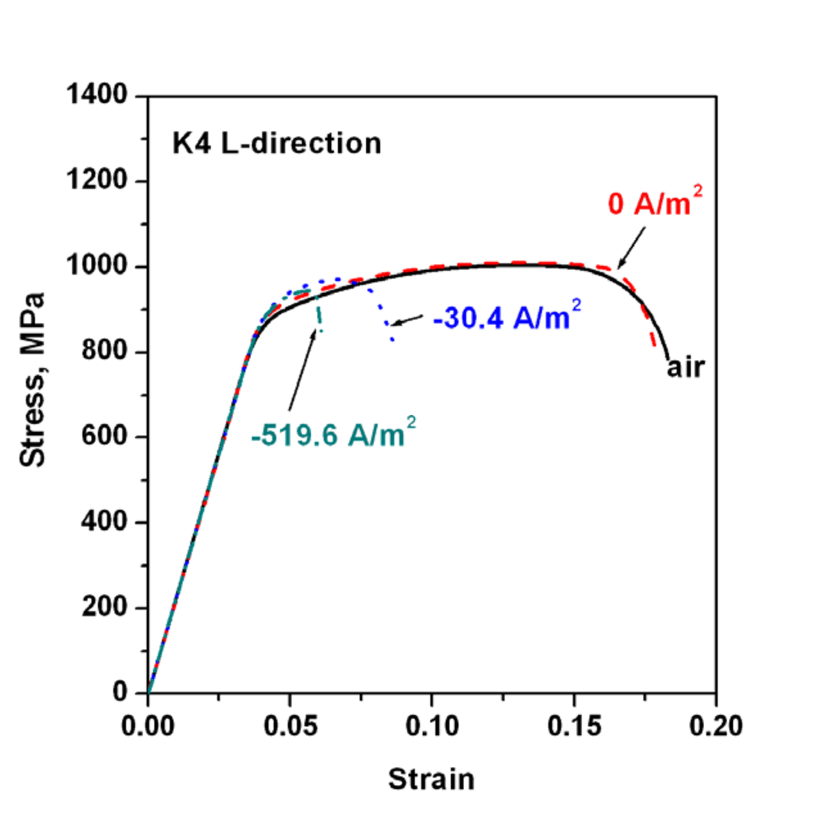
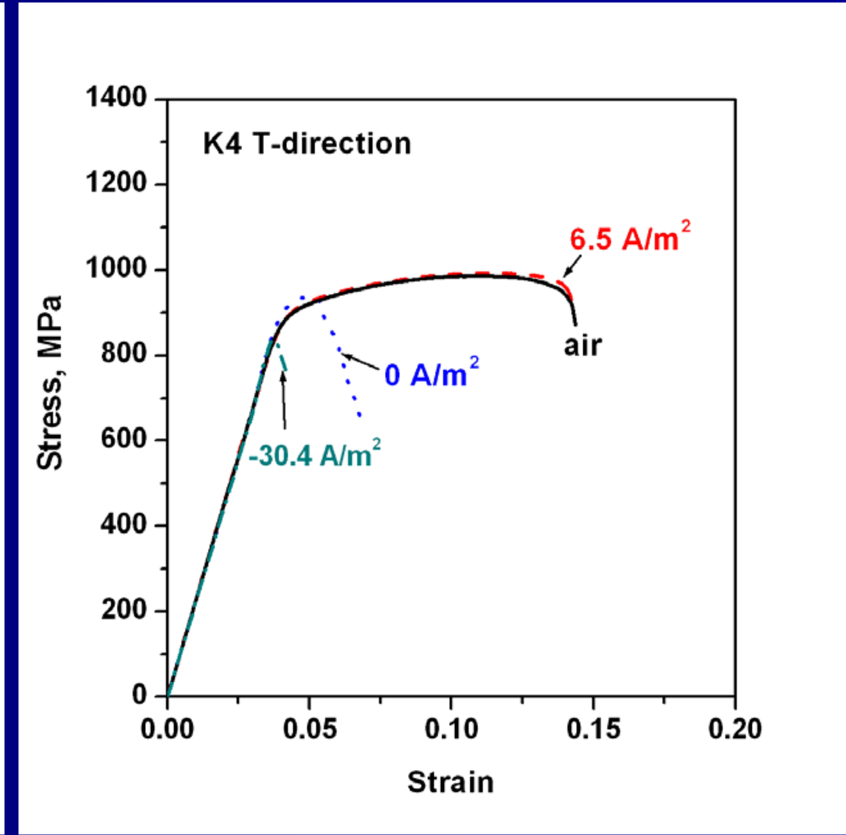
K4 ODS (19Cr-4Al)

L-direction

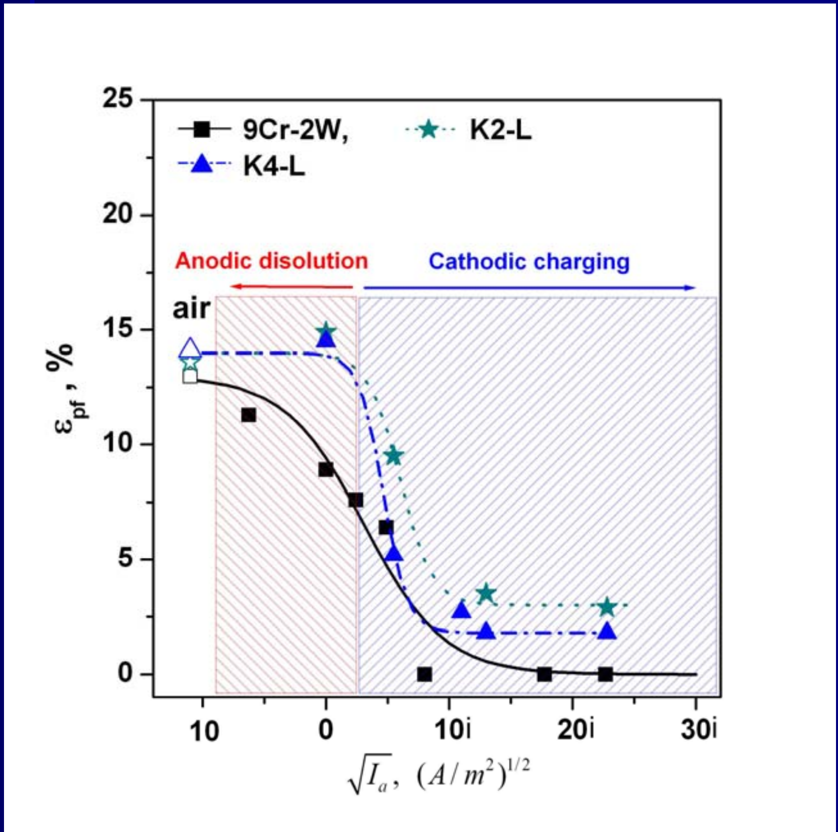


T-direction

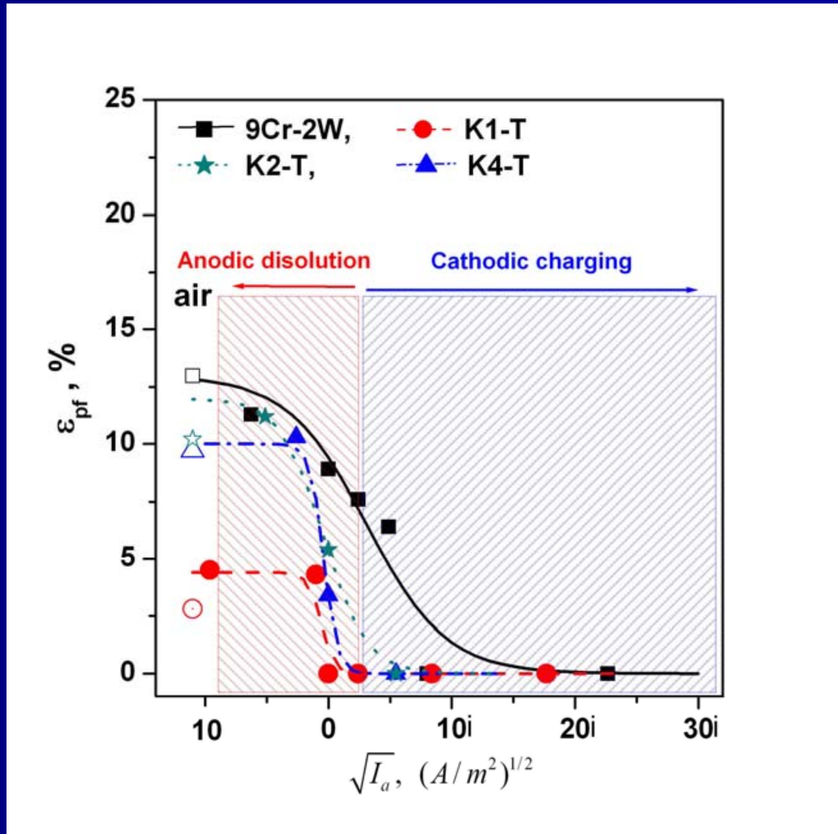


Transition of fracture strain (ε_{pf}) by hydrogen charging

L-direction



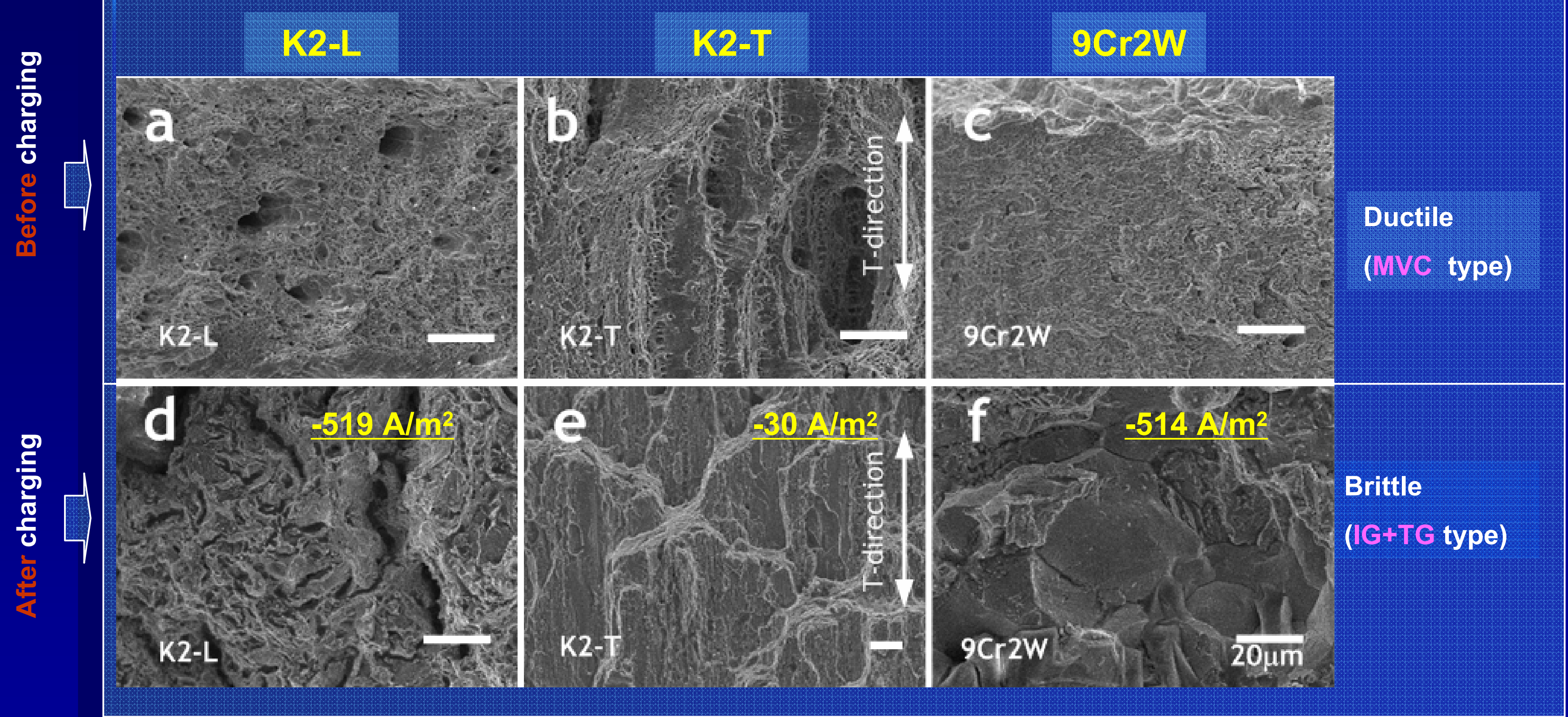
T-direction



The critical current density of K2-L, K4-L and a 9Cr2W was approximately -42.5, -23.0 and -4.0 A/m^2, respectively.

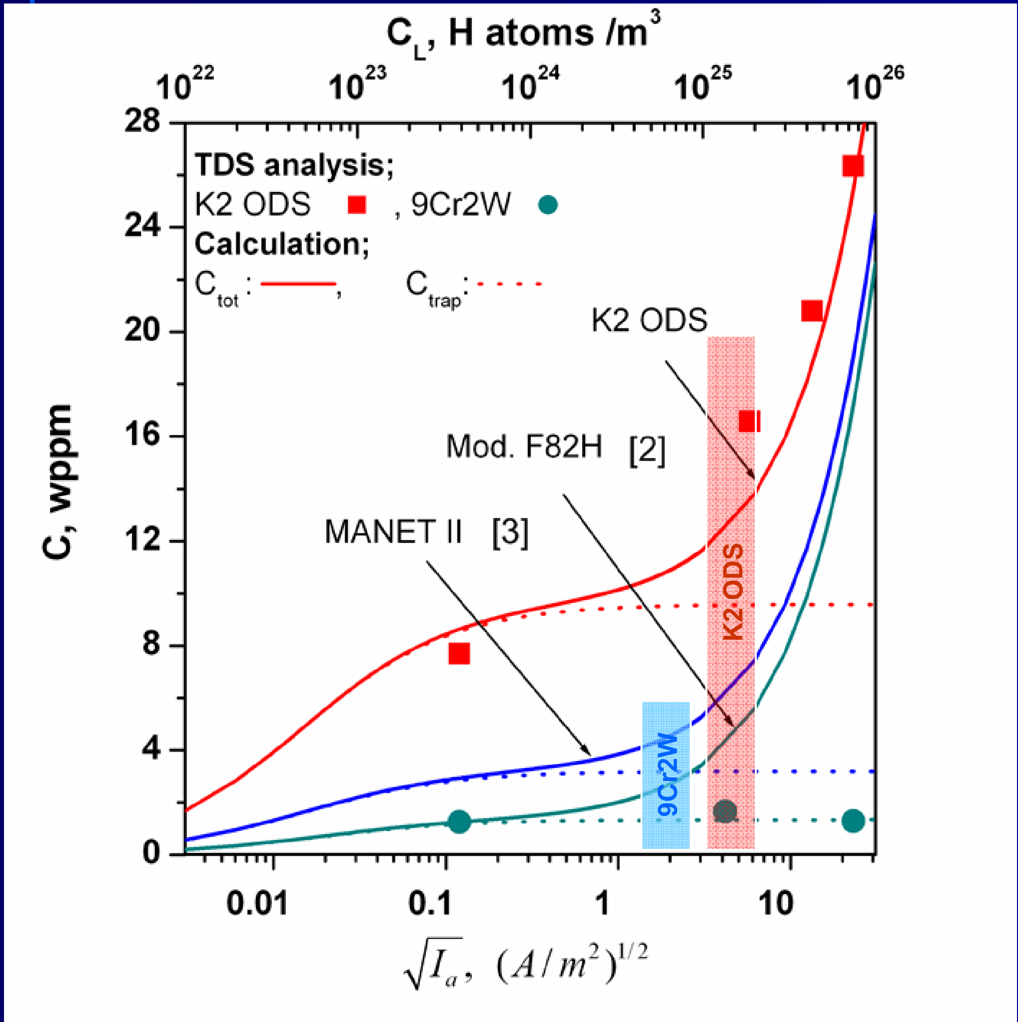
The critical current density of T-direction was almost 0 A/m^2, irrespective of the materials.

Changes of fracture mode



Change in fracture mode from **ductile shear rupture** to brittle **inter + transgrannular fracture** by H charging

Critical hydrogen concentration



H concentration in NISL and input current density in Fe iron [5].

$$C_L(Hatoms/gFe) = 1.3106\times10^{17}\sqrt{I_{In.}}(mA/cm^2) + 4.9645\times10^{16}$$

Critical hydrogen concentration of K2 ODS and 9Cr-2W steel is in the range of 10~12 and 1~2 wppm, respectively.

[5] J.L Lee, J.Y. Lee, Scripta METALL. 19 (1985) 341.

Thermal Aging Effects

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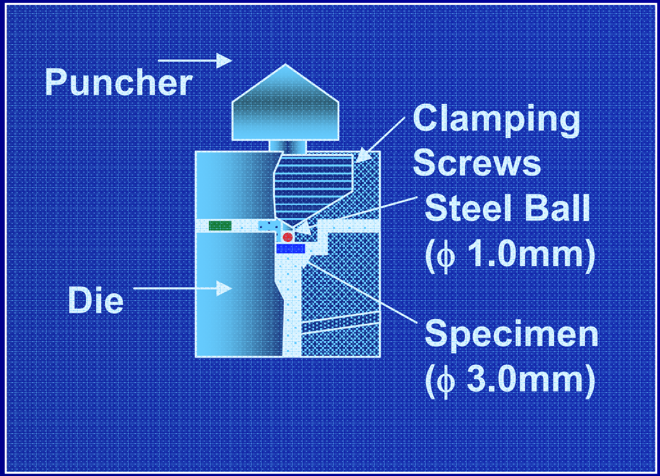
Thermal aging treatment and SP tests

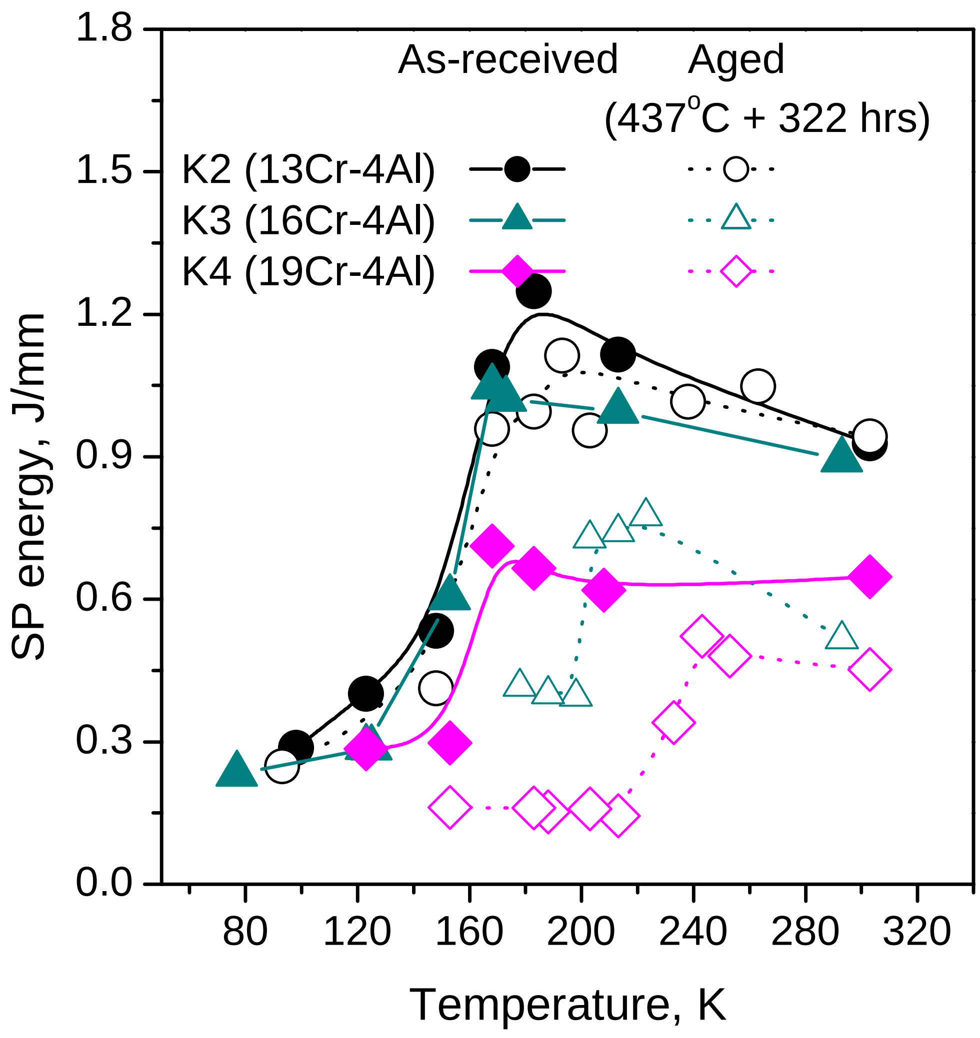
- Thermal aging treatment
  - from 430 to 475 C up to 1000 h

- Small Punch test
  TEM disk type (ϕ=3, t=0.25~0.27)
  Cross head Speed: 0.2 mm/min
  Test Temperature: from RT to 77K
  1 mm diameter steel ball

SP jig



Changes in SP-energy (437 C + 322 hrs)



SP-ΔDBTT

13 Cr (K2)	~10K
16Cr (K3)	~50 K
19Cr (K4)	~73 K

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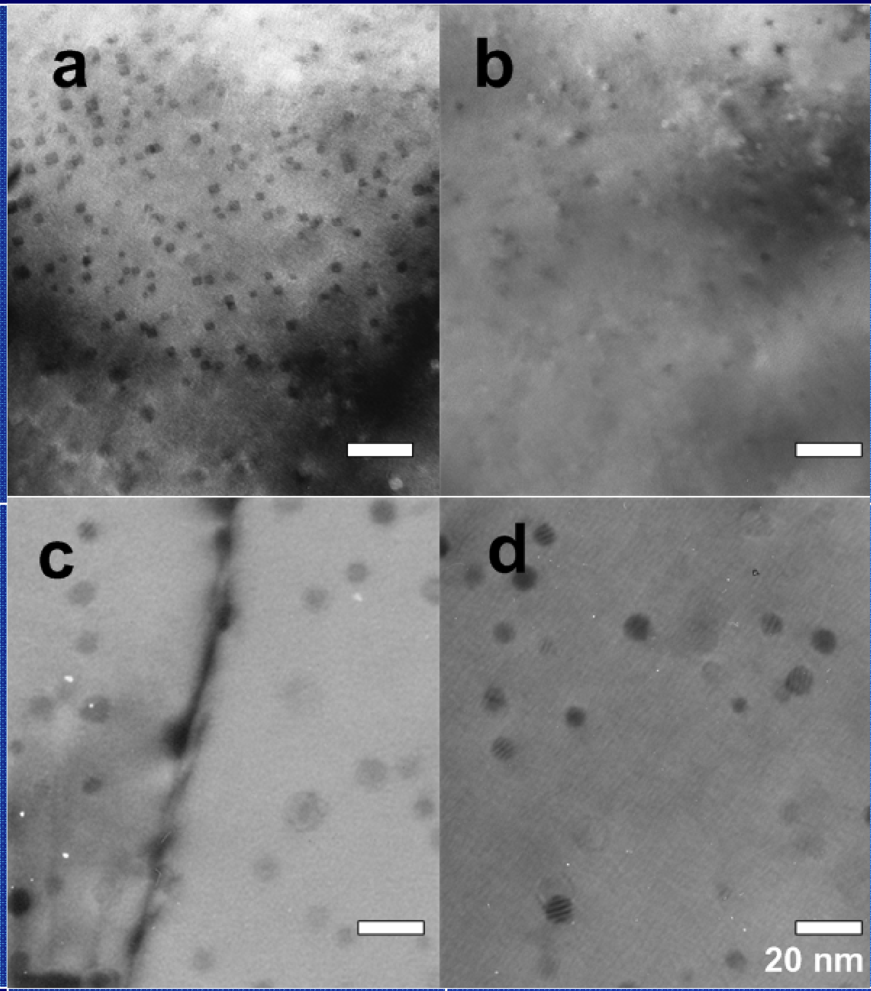
Thermally aged ODS steels
(437 C + 322 hrs)



	As-received	Aged
K1	a	b
K5	c	d

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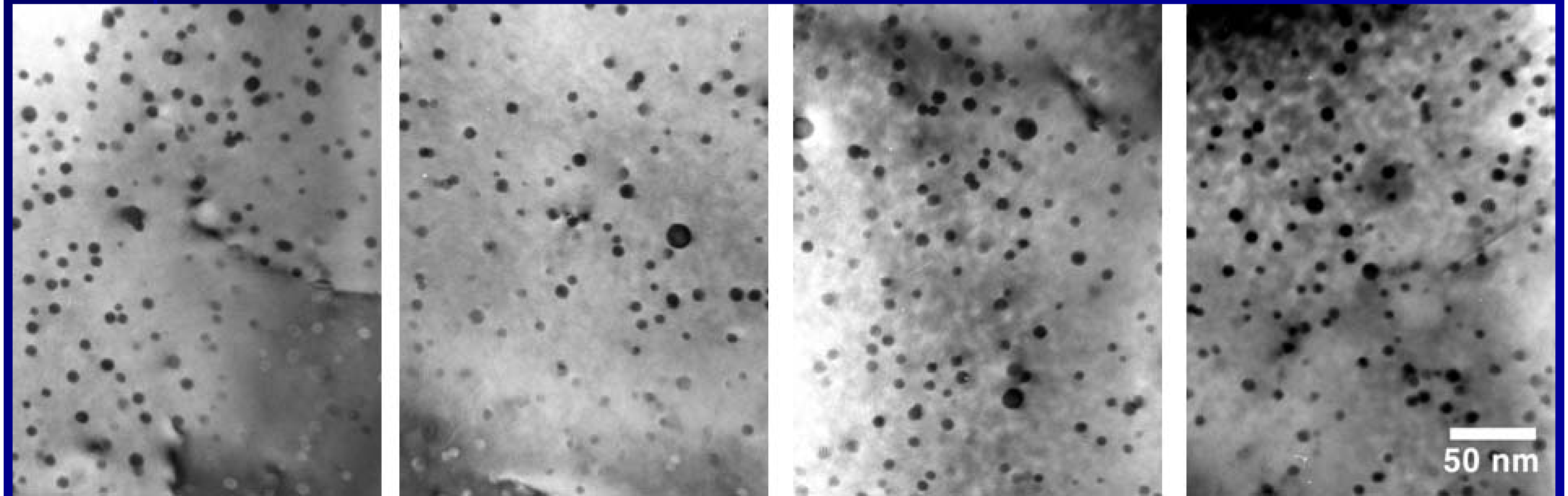
Formation of α′

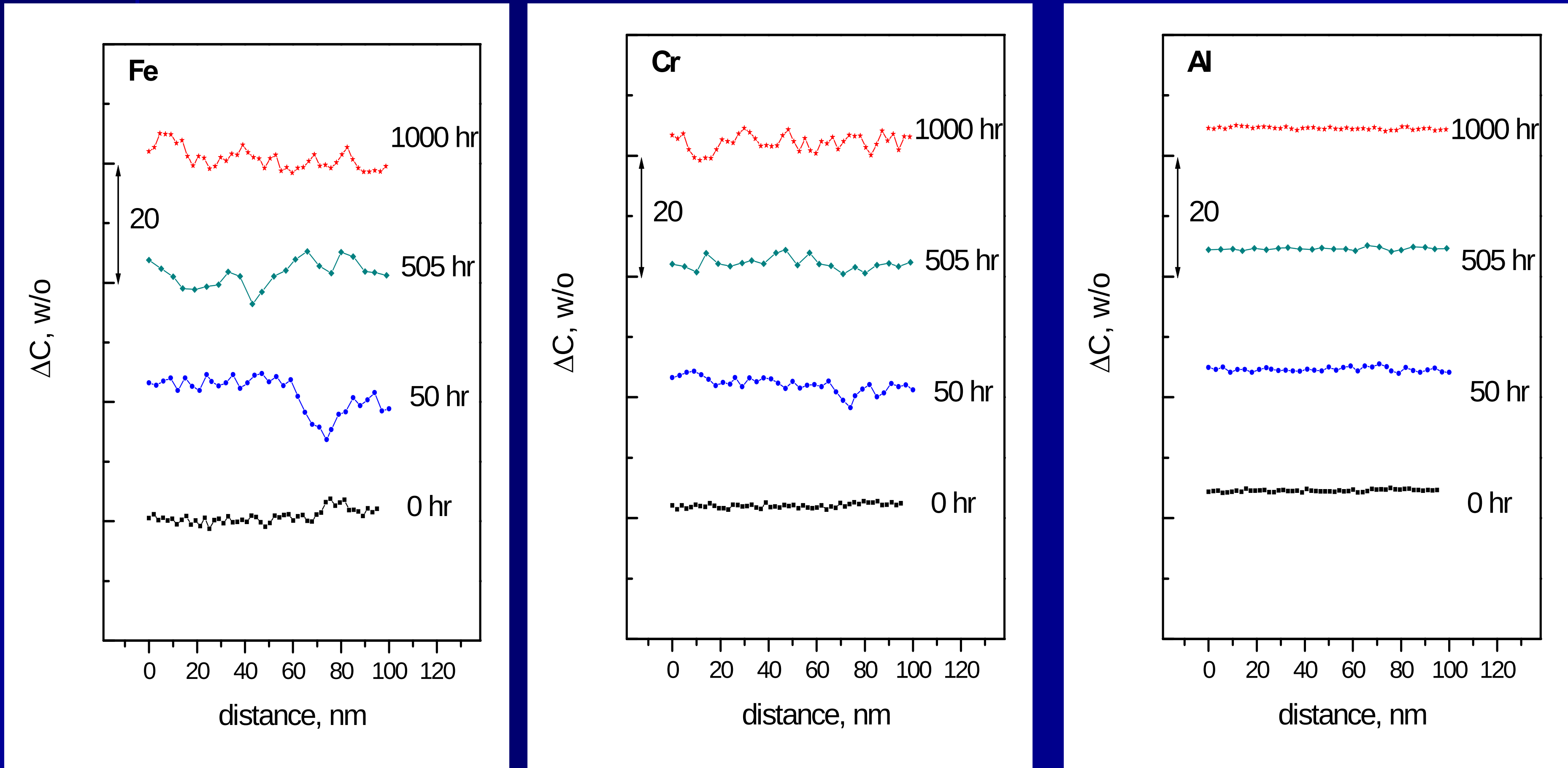
475 C Aging (K5 ODS)



10 hours | 50 hours | 505 hours | 1000 hours

Atomic fluctuation by thermal aging

475 C Aging (K5 ODS)



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Activation energy

- Arrhenius type

Q/R = 25843 (K1, K4 ODS)

= 27468 (K3 ODS)

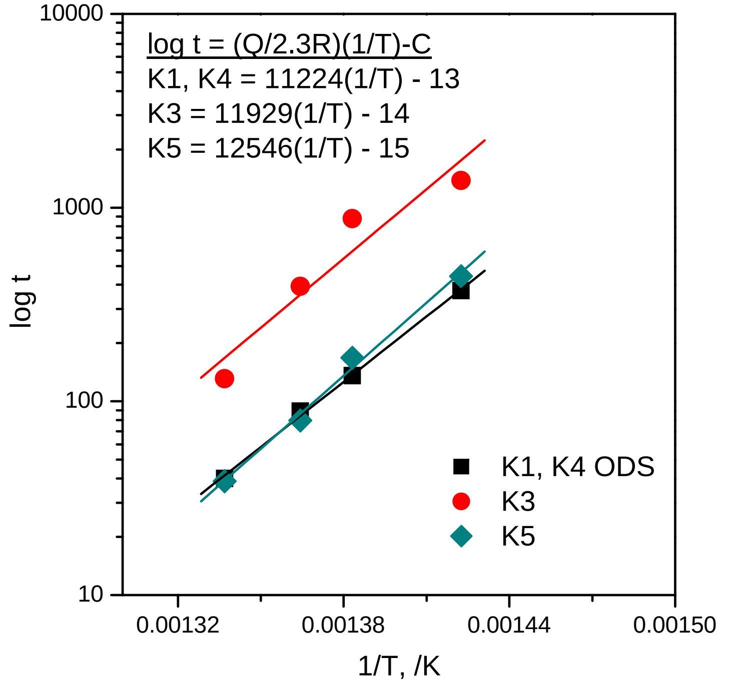
= 28889 (K5 ODS)

Activation energy

Q = 214 kJ/mol (K1, K4 ODS)

= 228 kJ/mol (K3 ODS)

= 240 kJ/mol (K5 ODS)



***The activation energy for diffusion of Fe and Cr in a Fe-26Cr alloys was 211 and 203 kJ/mol, respectively [1].**

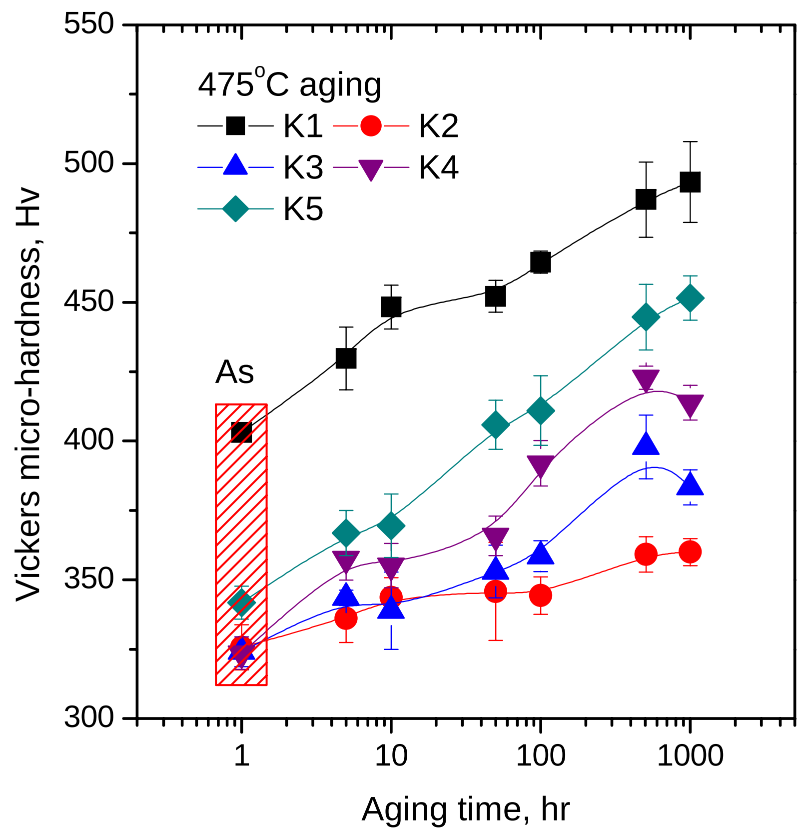
The activation energy for Cr diffusion was 229.8 kJ/mol [3]

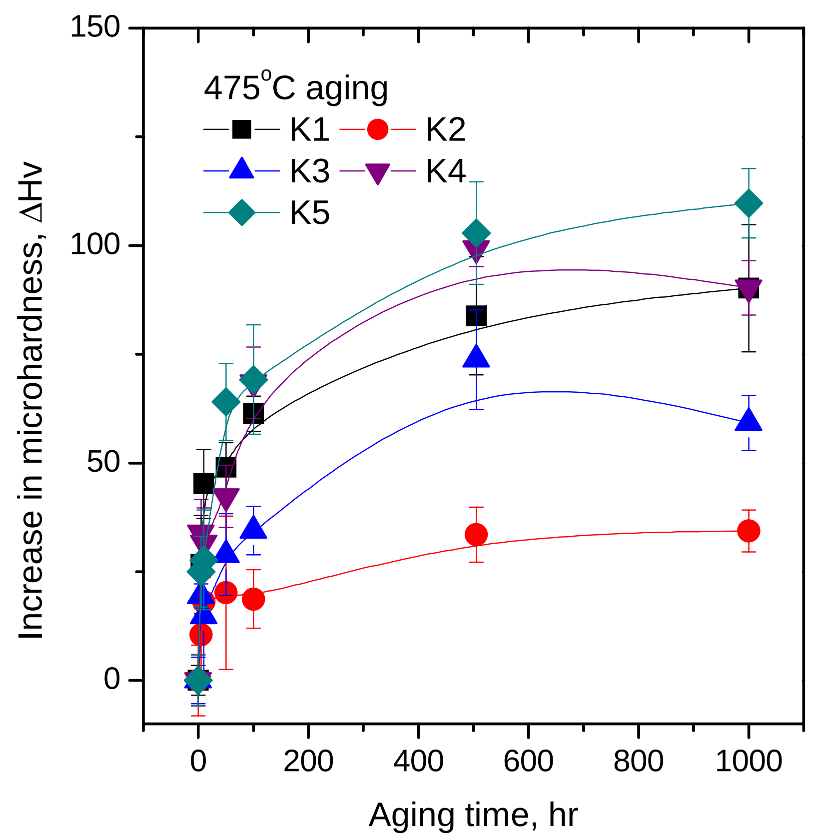
[1] Browdes EA, Brook GB, editors. Smitells metals book. Seventh ed. Heinemann: Butterworth; 1992, p. 13

[3] T. Heumann and H. Böhmer, Arch. Eisenhűttenw., 1960, Vol. 31, p. 749

Increase in Micro-hardness

475 C Aging





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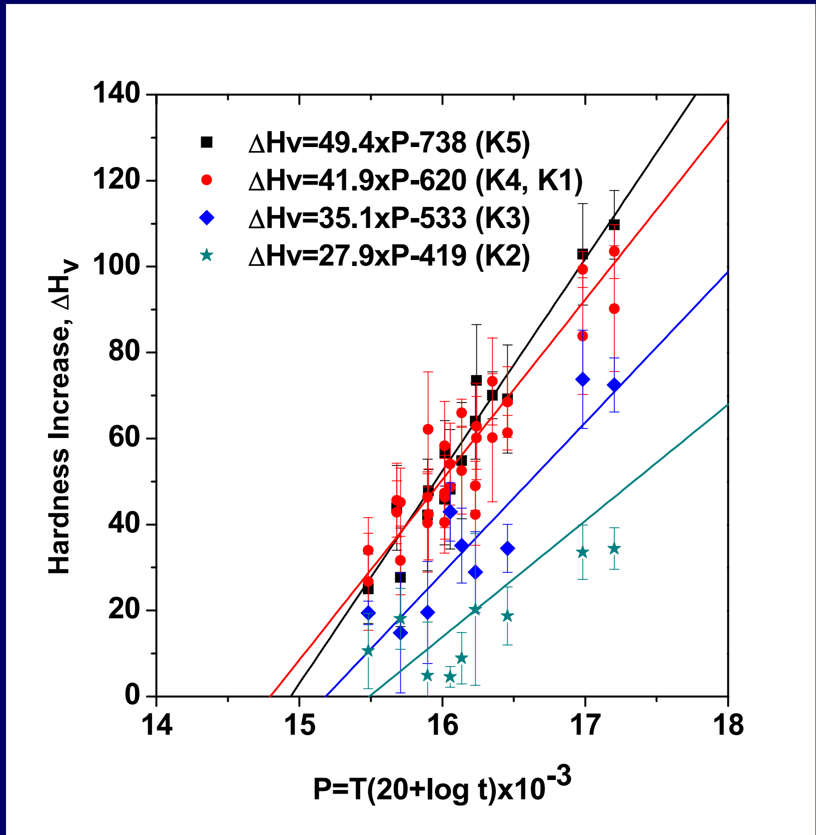
Generalized Hardening Formula



ΔHv = 49.4 x P – 738 (K5 ODS)

ΔHv = 41.9 x P – 620 (K1, K4)

ΔHv = 35.1 x P – 533 (K3)

ΔHv = 27.9 x P – 419 (K2)

$\Delta Hv = (2.37Cr-3.02)xT(20+\log t)x10^{-3} -(34.8Cr-31.5)$

(430 < T [K] < 475 C, 5 < t [hour]< 1000, 13 < Cr [w/o] < 22)

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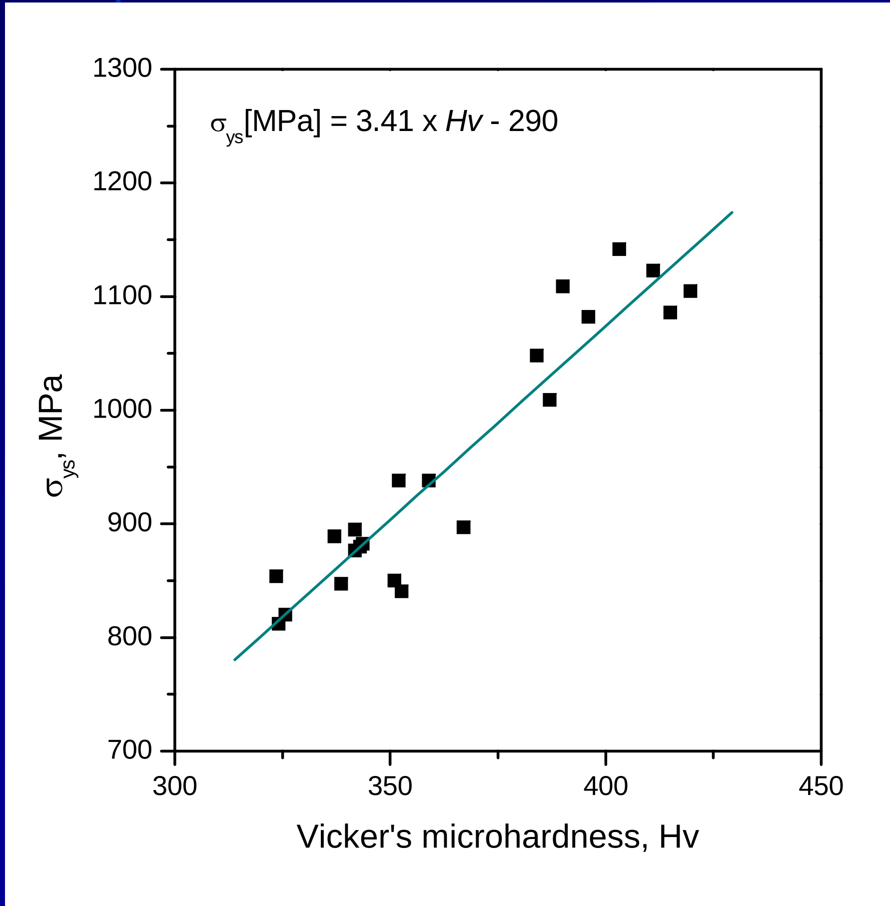
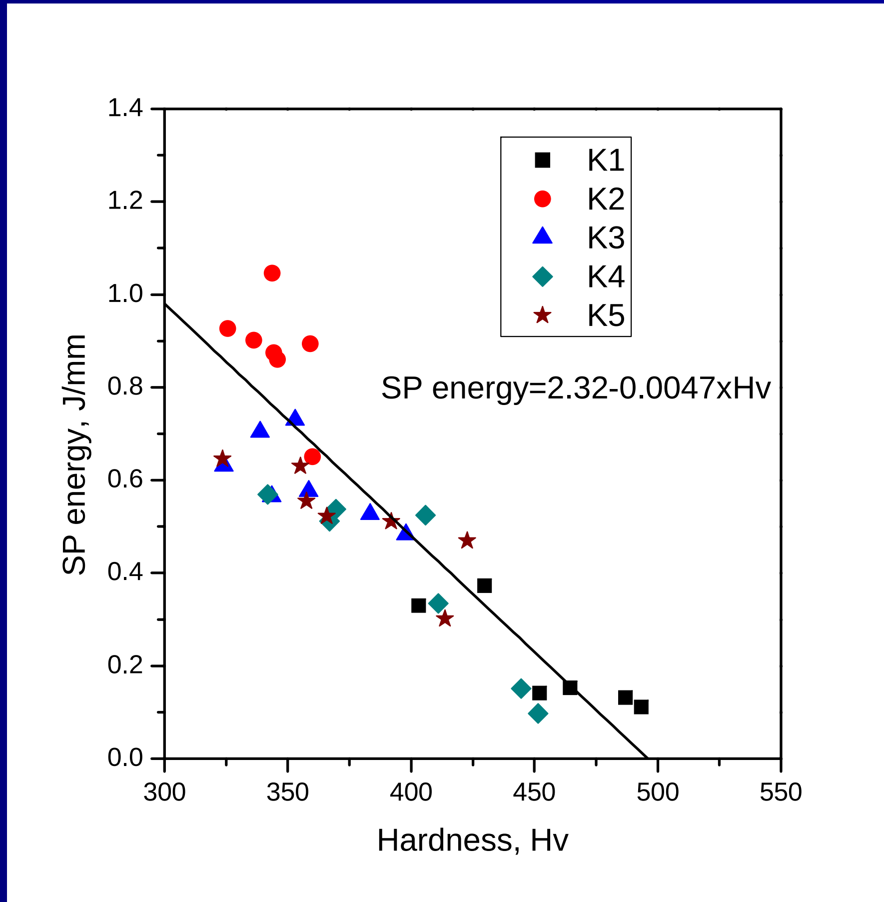
Relationship yield, SP energy with ΔHv





$\Delta\sigma_{ys}$ [MPa] = 3.41 x ΔHv , (0 < ΔHv <120)

Summary

- Cathodic hydrogen charging considerably reduced the tensile ductility of ODS steels accompanied by the change of fracture mode from ductile shear rupture to intergrannular and quasi-cleavage fracture.

- The critical hydrogen concentration required to induce brittle cracking in ODS steels is in the range of 10-12 wppm that is *almost one order higher value* than the 9Cr-2W RMS.

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- High Cr ODS steels are experienced significant thermal aging embrittlement at temperatures from 430 to 475 C caused by the formation of Cr-rich coherent ferrite phase, α' phase.
- The hardening relationship at current test conditions can be obtained successfully as a function of Cr content and aging time.