Charles Hatchett Award 2017
of the Institute of Materials, Minerals and Mining (IOM3)

Direct observation of niobium segregation to dislocations in steel

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Niobium in steels

Niobium (Nb) is very important alloying element in steel, because it is used for grain refinement through the retardation of recrystallization in the hot-rolling process and cold-rolling annealing process.

1) Solute drag effect by solute Nb atoms by Cahn (1962)

2) Pinning effect by Nb carbonitride (NbC, NbN) precipitates by Weiss and Jonas (1972)

Based on calculations, the former is more effective in ferrite, while either the former or the latter may be more effective in austenite phase, depending on the recrystallization temperature. by Hutchinson (2008)

Nb in solid solution also impeded the dislocation movement and significantly retarded the recovery of dislocations in steel. However, the mechanism has remained unclear.

<Hypotheses>

- Nb-vacancy interaction decreasing the self-diffusion of Fe
- Pinning by fine NbC clusters or Nb-C dipoles
- Direct interaction between Nb atoms and dislocations

Direct interaction between C and dislocation

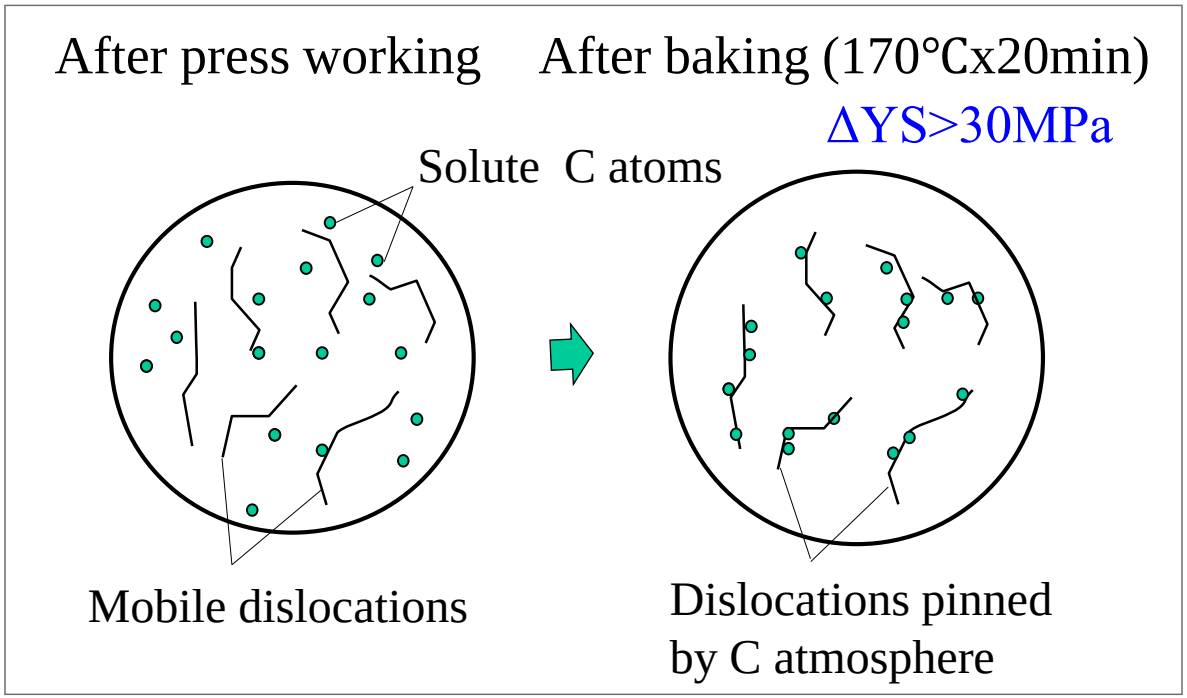
Carbon Cottrell atmosphere (1948)

Cottrell and Bilby (1948)

They developed the new idea that dislocations are pinned by carbon atoms segregating around the dislocations due to the elastic interaction, and they successfully explained the yielding and strain ageing of iron, theoretically.

<Application to steel product>

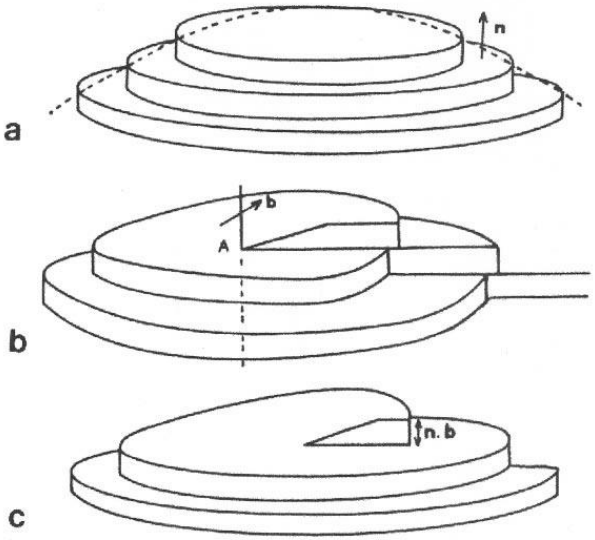
Bake-hardening steel
(BH steel)



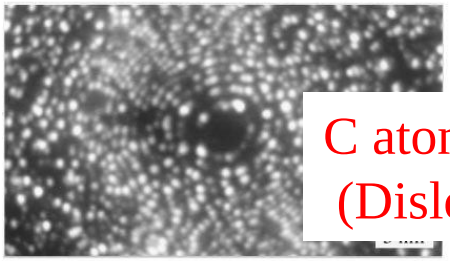
Direct observation (2000)

Cottrell atmosphere was actually observed with atom probe tomography (APT) and field ion microscopy (FIM).

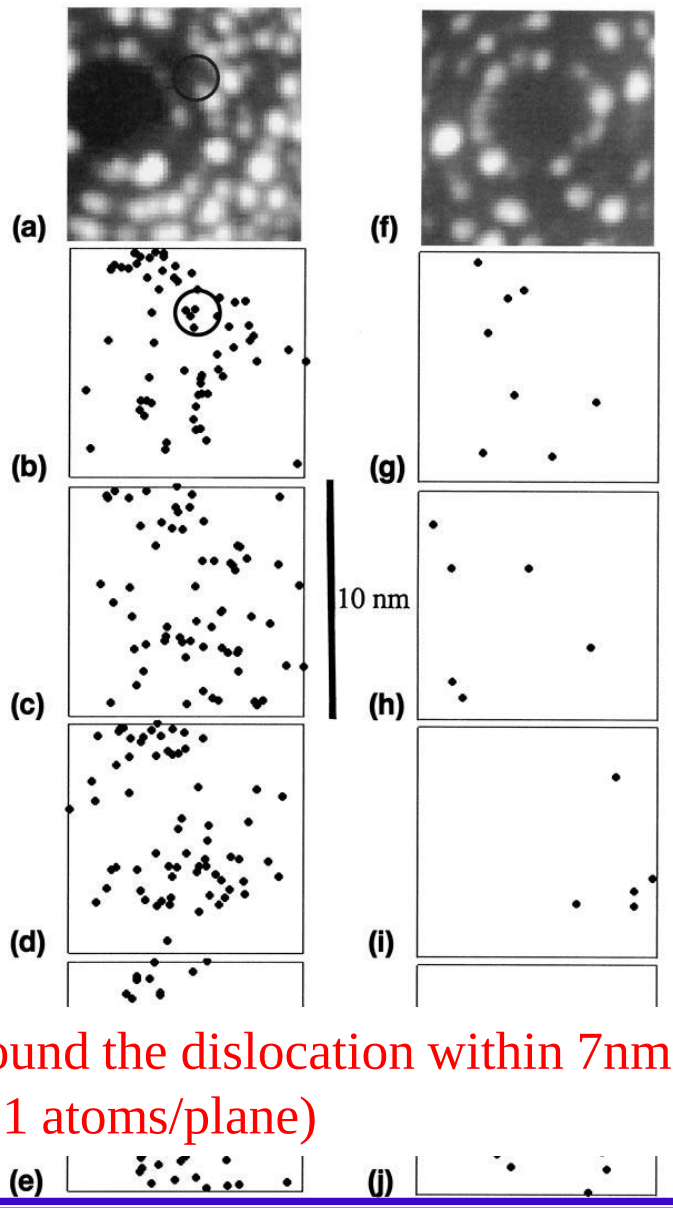
Wilde *et al*. (2000)



Screw dislocation



FIM image



C atoms were enriched around the dislocation within 7nm.
(Dislocation excess: 21±1 atoms/plane)

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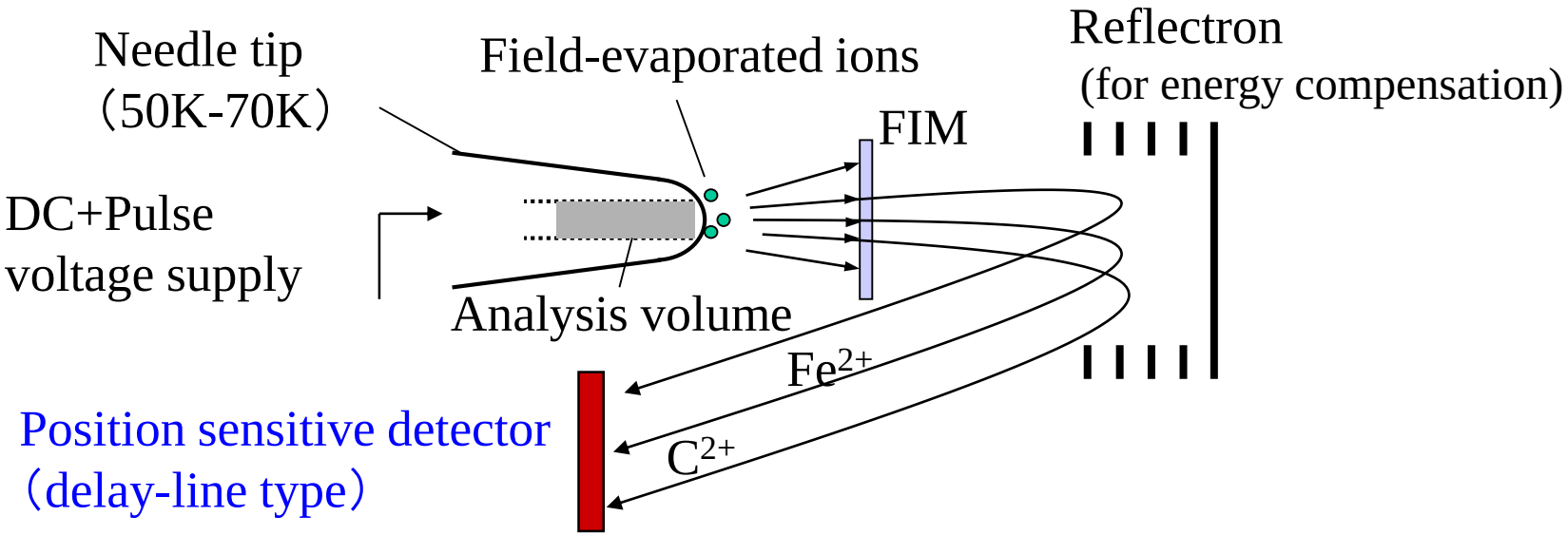
Atom Probe Tomography (APT)



<Advantage> Detection of every element including light elements (H, D, B, C)

High spatial resolution (～lattice spacing size)

<Disadvantage>

Dislocations are not directly observed.

Objective

Nb atoms in solid solution significantly retard the recovery of dislocations in steel.

The mechanism has remained unclear.

- Nb-vacancy interaction decreasing the self-diffusion of Fe
- Pinning by fine NbC clusters or Nb-C dipoles
- Direct interaction between Nb atoms and dislocations

Nb added ferritic stainless steel

～The steel does not contain solute C and N,
however the steel has high performances in high temperature use.

→ Effect of solute Nb atoms

Objective

To investigate the state of Nb atoms in the steel, and to clarify the presence of direct attractive interaction between Nb atoms and dislocations.

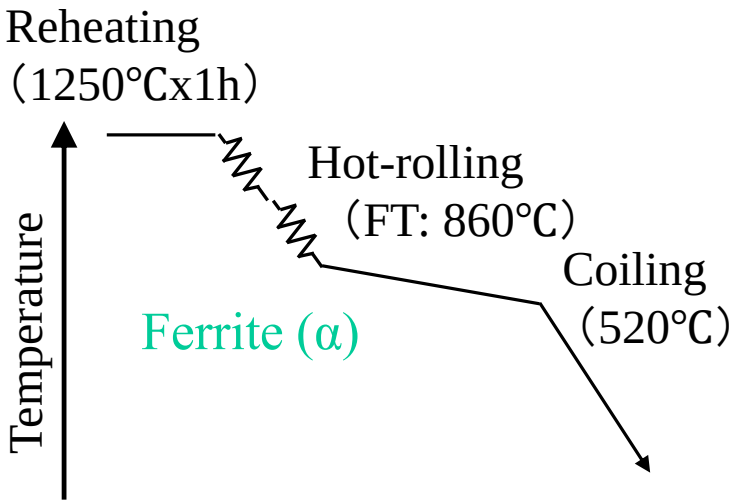
Nb added ferritic stainless steel

The steel is actually applied for exhaust manifold in the automotive industry because of its high performance against thermal fatigue, where the proof strength is sufficiently maintained under repeated heating cycles（>700℃）.

	C	Si	Mn	P	Cr	Mo	Cu	Ti	Nb	N	B
mass%	0.008	0.21	1.02	0.025	16.95	0.31	1.25	0.12	0.53	0.013	0.0008
at.%	0.037	0.42	1.04	0.045	18.2	0.18	1.10	0.14	0.32	0.052	0.0041

Sufficient amounts of Nb and Ti were added to scavenge solute C and N.

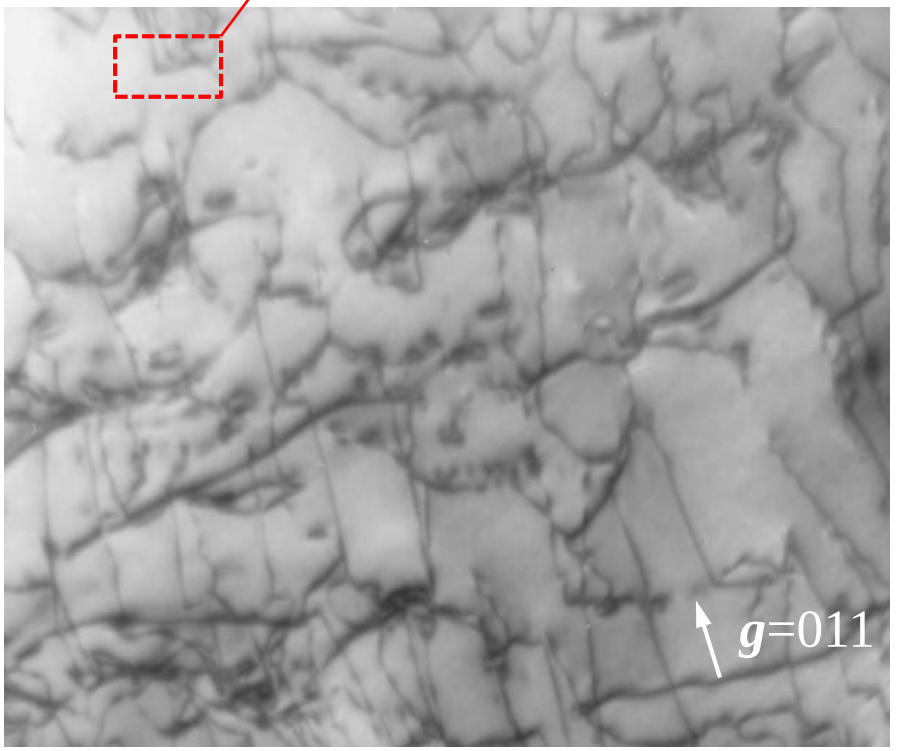
Nb+Ti >> C+N
(0.46at%) (0.09at%)



The steel hardly contains solute C and N.

Yield strength: 515MPa
Tensile strength: 571MPa

TEM micrographs



Fine particles locking the dislocations are not observed.

The dislocations are almost homogeneously distributed in grain.

Dislocation number density: ～1.8 x10^{10} cm^{-2}

→ Dislocation line of about 30nm is included in dataset (5 million atoms) on average.

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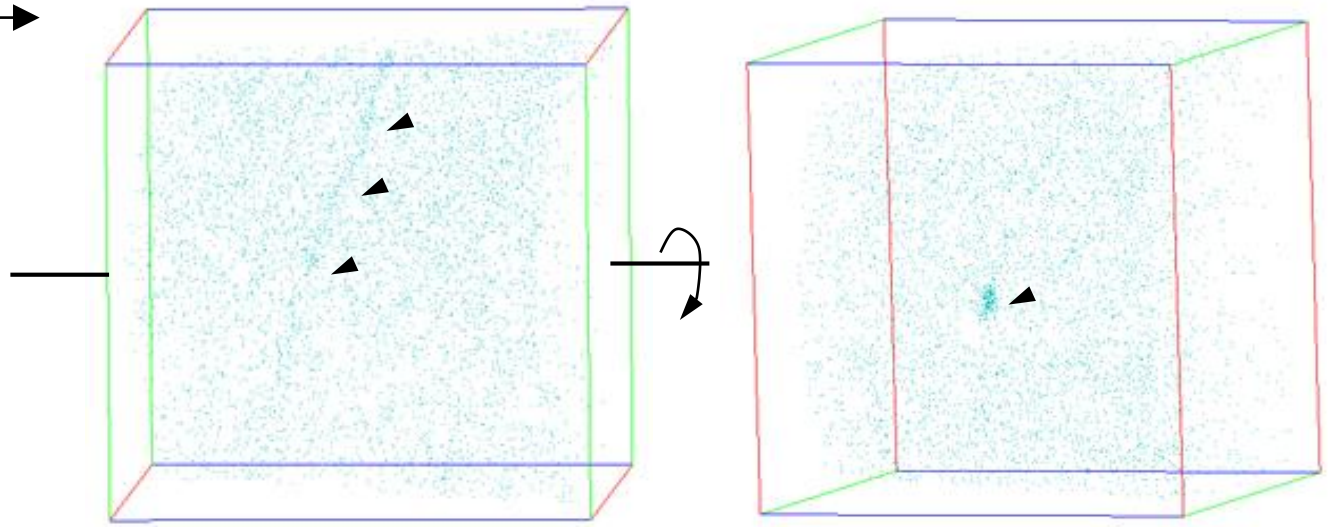
Solute Nb distribution in grain

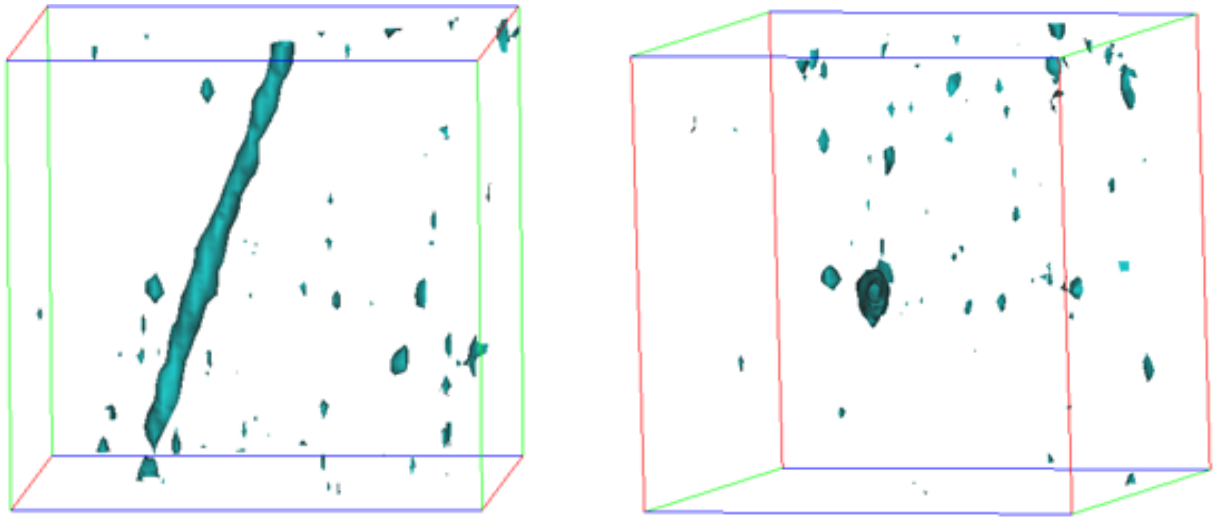
Probing direction →

44nm x 42 nm x 44nm

Nb atom map



Iso-concentration surface (1.2%Nb)



Nb enriched region is observed as a straight line.
Neither C nor N was observed in the region.

→ Nb decorated dislocation

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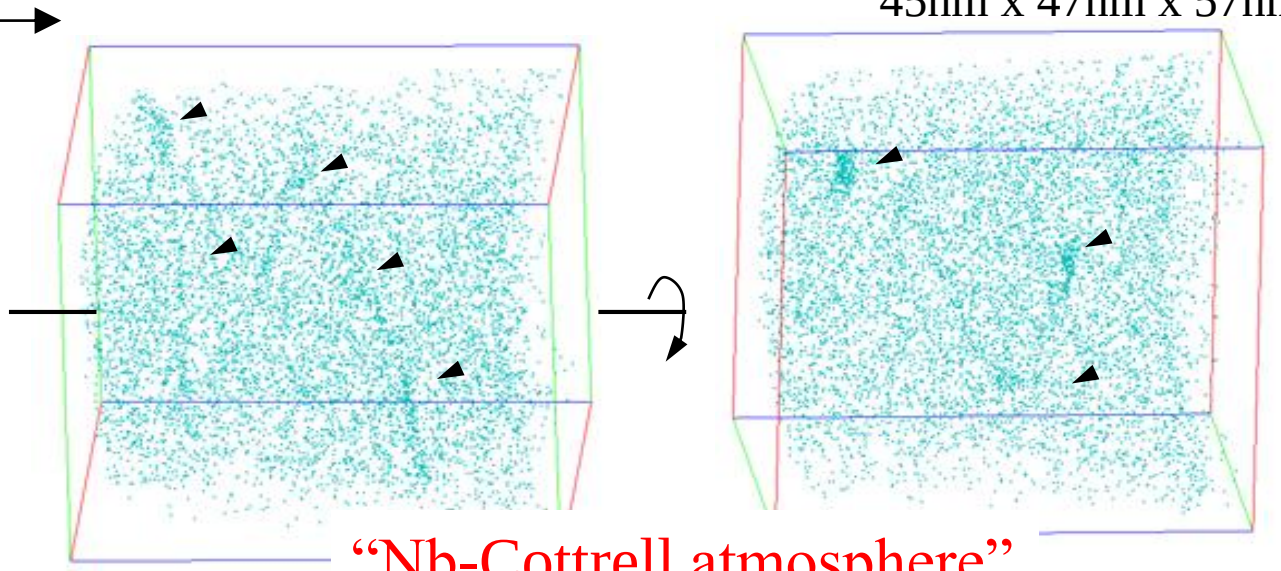
Solute Nb distribution in grain (other region)

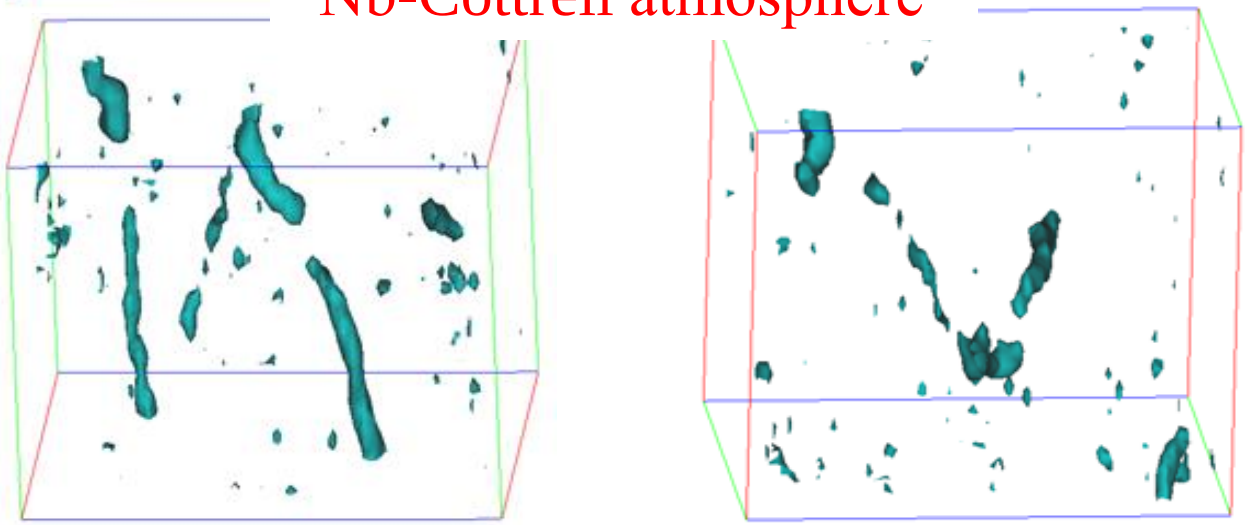
45nm x 47nm x 57nm

Nb atom map



"Nb-Cottrell atmosphere"

Iso-concentration surface (1.2%Nb)



Nb decorated dislocations are observed as curved lines.
The segregation amount varies depending on the orientation of dislocation line.

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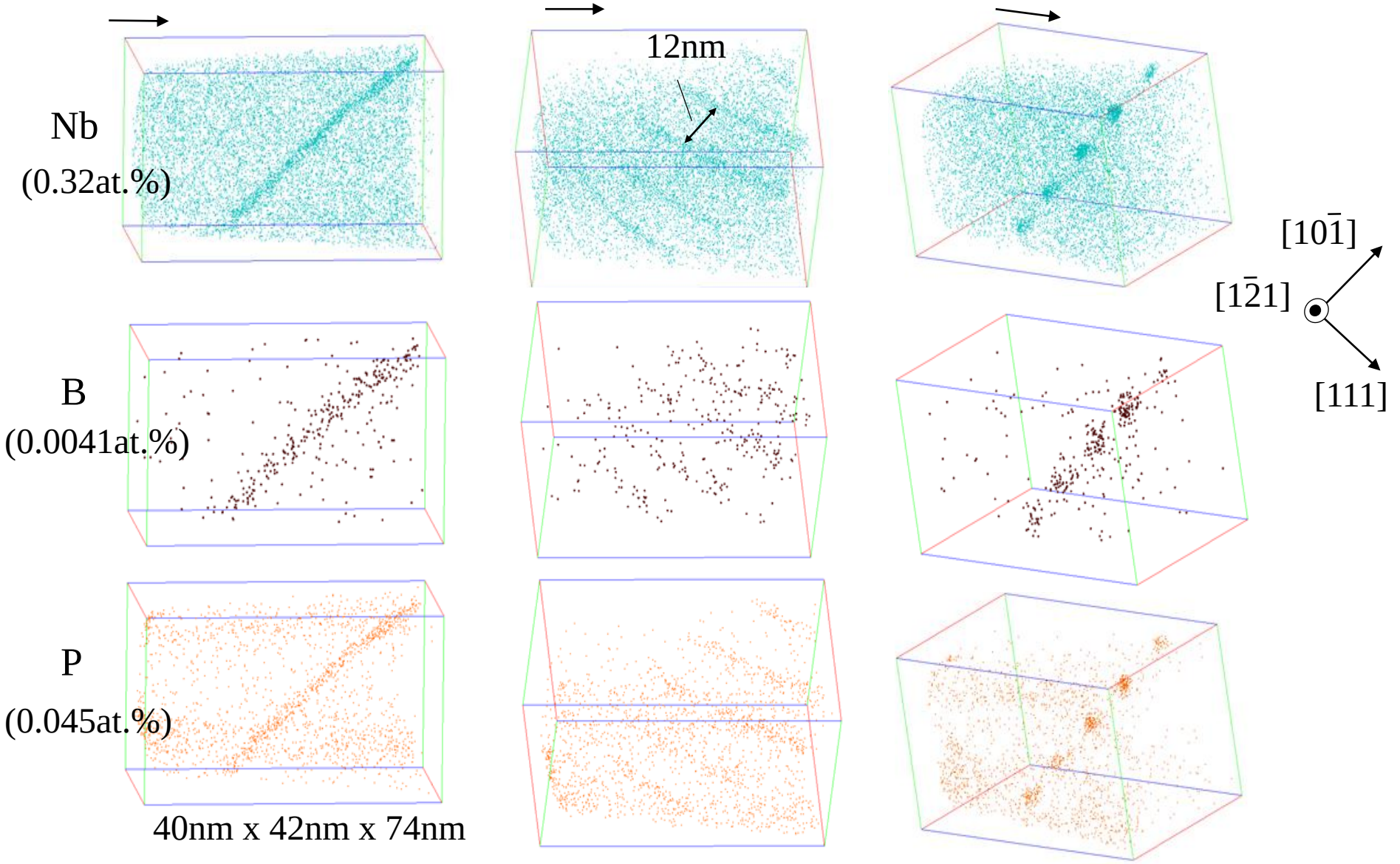
Low-angle grain boundary (dislocation wall)



Nb decorated straight dislocations are arranged in a row at intervals of 12 nm.

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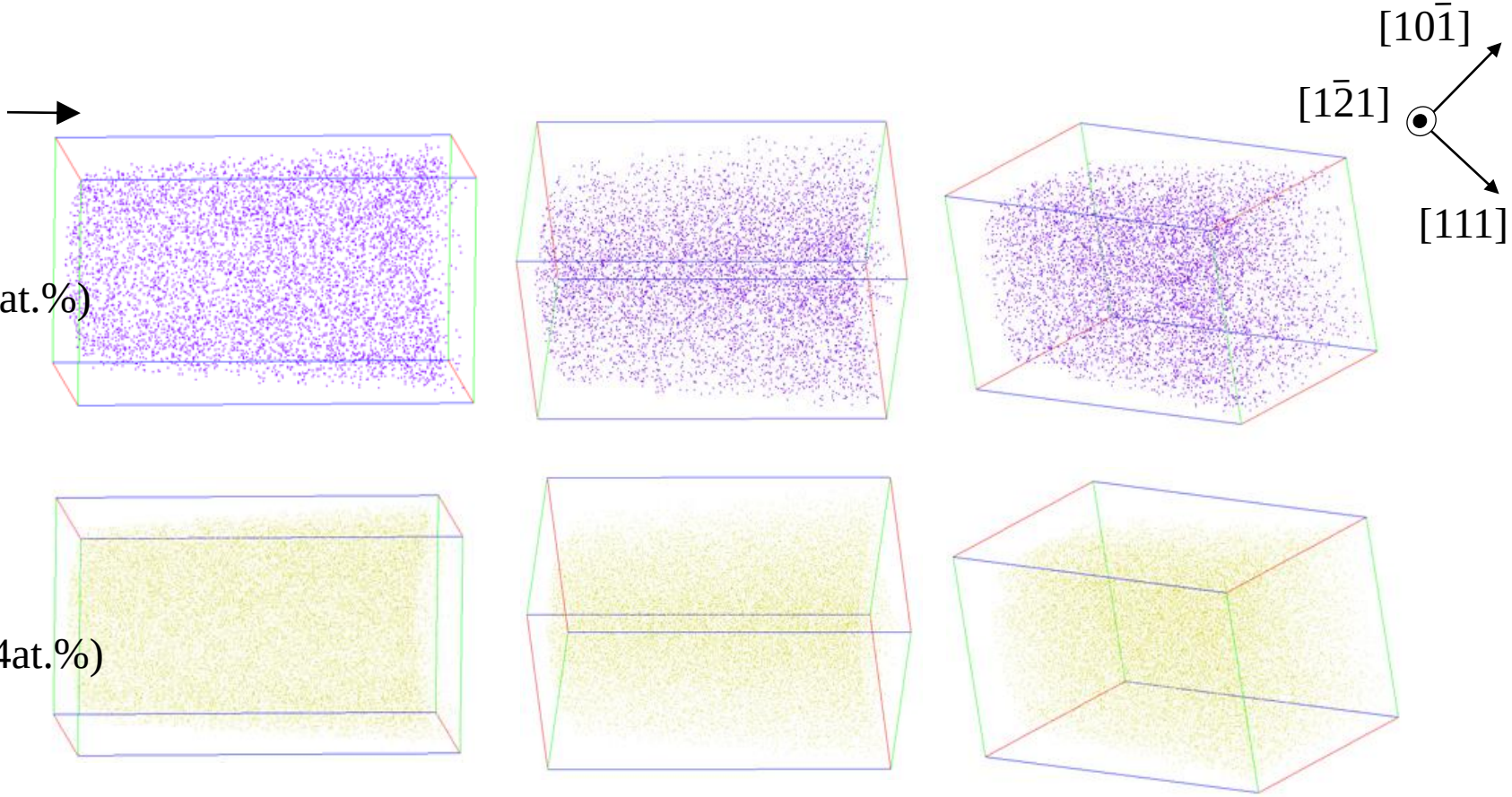
Low-angle grain boundary



Mn and Mo are not segregated around the dislocations although the content of Mn is much higher than that of Nb.

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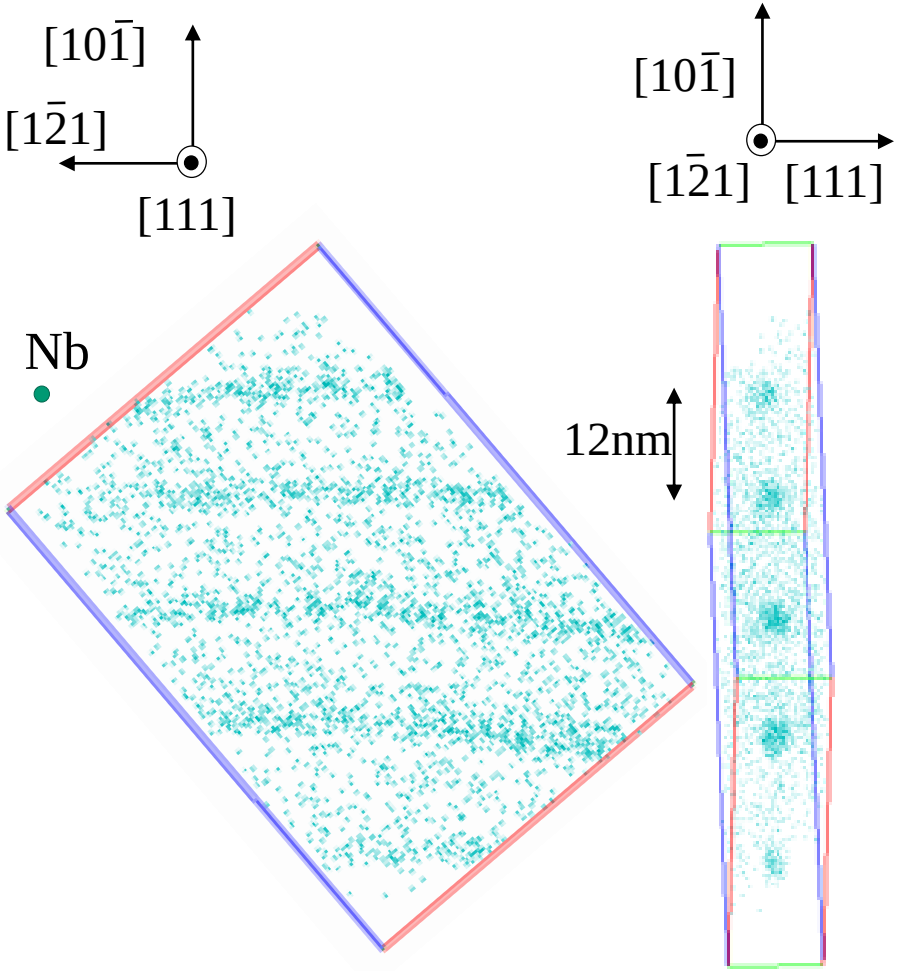
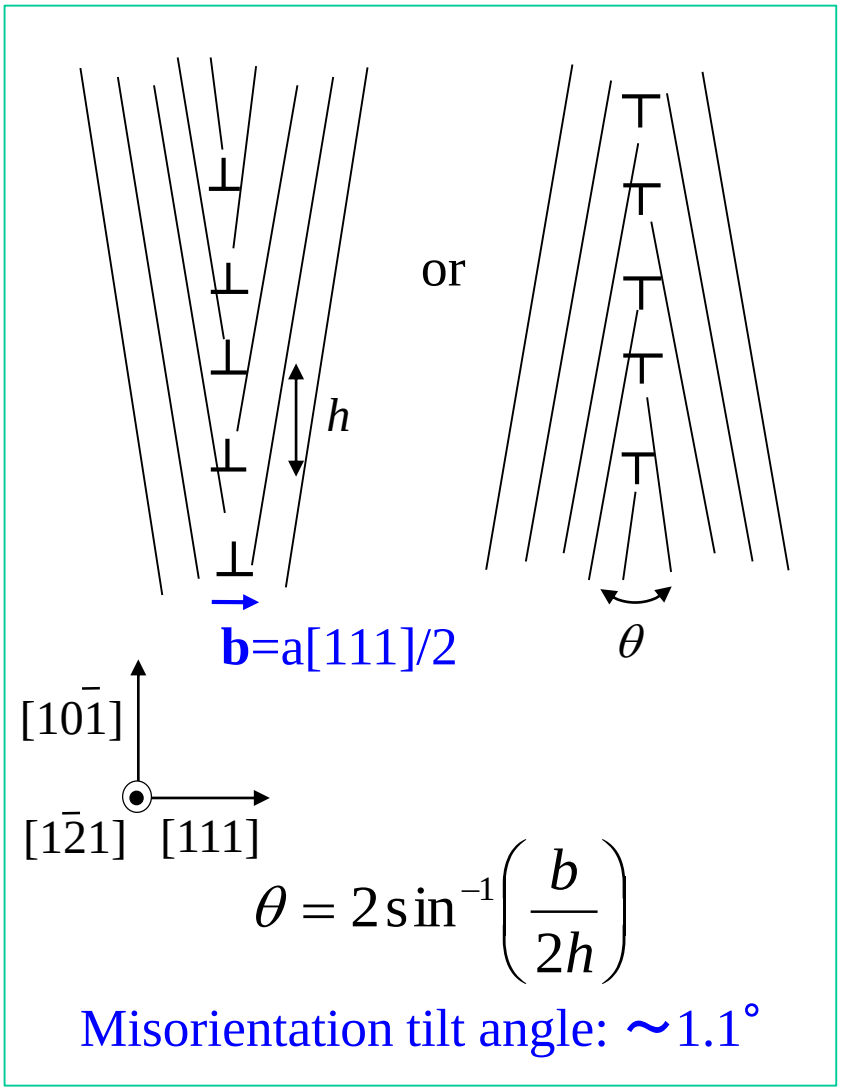
Characterization of dislocation and boundary





Low-angle tilt grain boundary on (111), composed of pure edge dislocations

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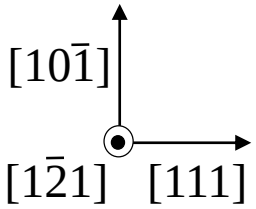
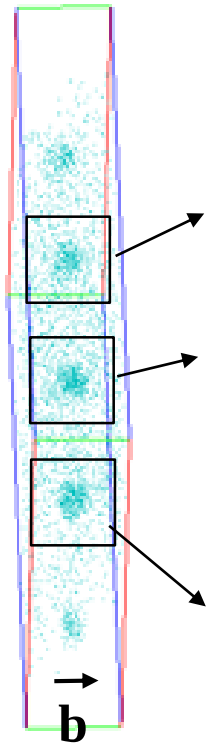
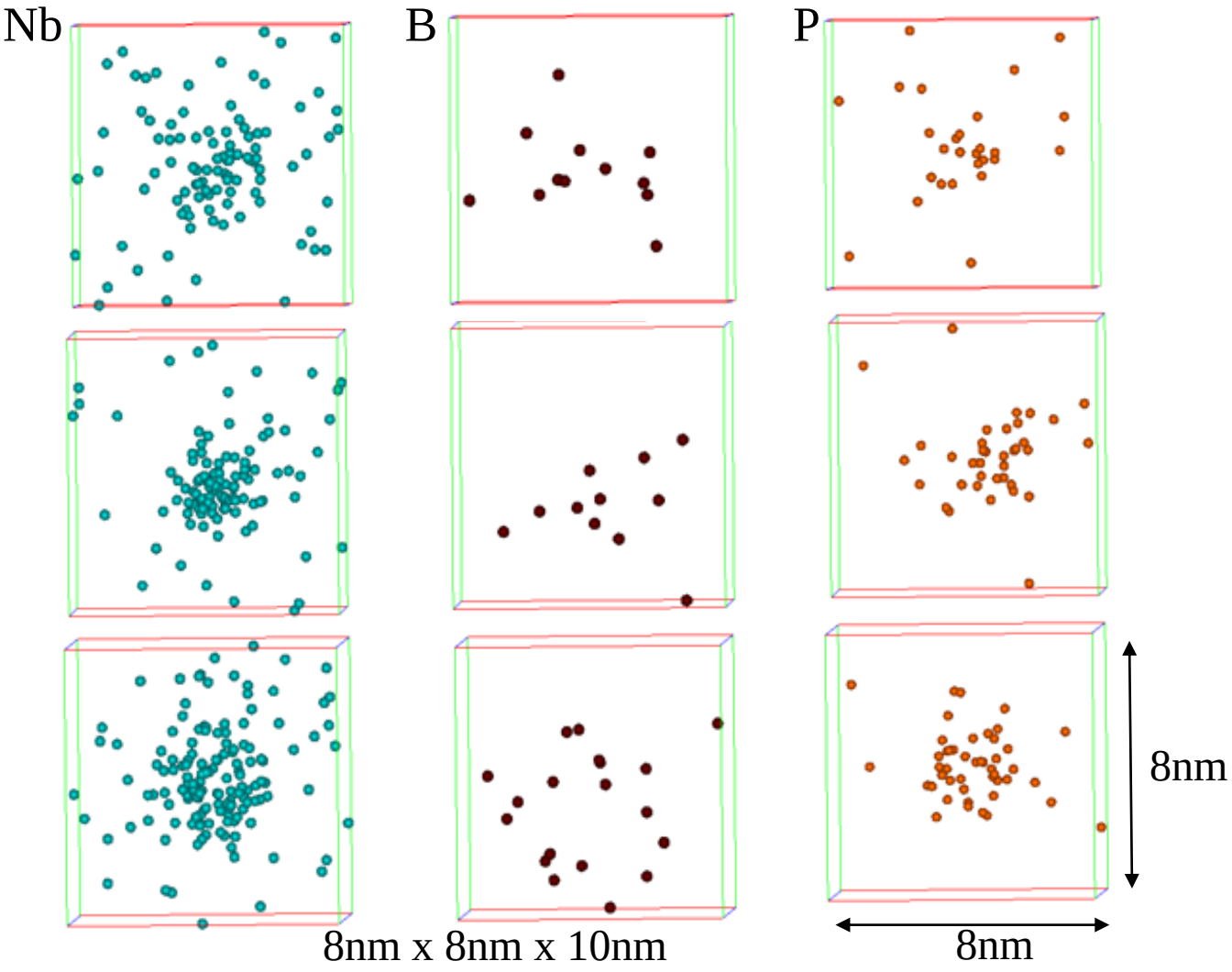
Distribution of segregated atoms

Pure edge dislocation（**b**=a[111]/2）







Most of the excess Nb atoms are observed within a small circle 2～3 nm in diameter.

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Quantitative estimation of dislocation segregation

Element		Nb	B	P	Mo	Mn
Dislocation excess (atoms/nm)	Edge dislocations in dislocation wall	21.9 ± 0.9	4.1 ± 0.4	7.5 ± 0.5	—	—
	Single dislocations	7.2-16.8	1.4-1.9	2.0-2.2	—	—

Mixed dislocation

(*Detection efficiency: 0.35)

The segregation amount to dislocation depends on the type of dislocation.
Edge dislocation has larger dislocation excess than screw or mixed dislocations.

The extent of the Nb enriched region (< 2nm) is smaller than that of the C Cottrell atmosphere (< 7nm) in the strain field of dislocation.

Nb atoms segregate in the dislocation core, different from C Cottrell atmosphere.

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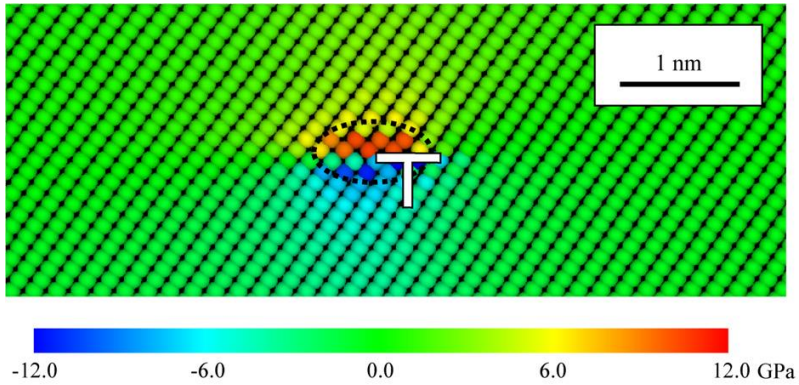
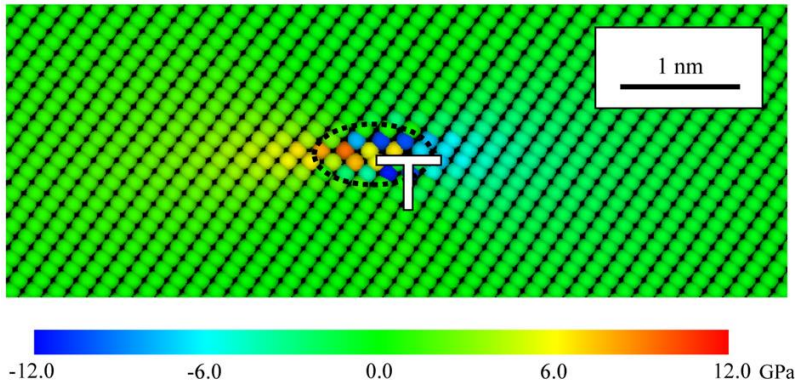
Nb-segregation site and interaction energy

Taketomi *et al*: Acta Mater. 56 (2008) 3761.



(a) Hydrostatic stress (σ_h)



(b) Shear stress (τ_{xy})

Number of substitutional sites in the {112}<111> edge dislocation core: 8 / (112) plane (normal to the dislocation line)

Number of sites with expansive strain: 4 /(112)

Langmuir-Mclean model（equilibrium state）

$$\frac{X_b}{X_{b0}-X_b}=\frac{X}{1-X}\exp\left(\frac{-\Delta G_b}{RT}\right)$$

X_b: GB concentration of segregating atoms

X_{b0} : the saturated value of X_b

X: atomic fraction of the element in the matrix

ΔG_b: Gibbs free energy of segregation

(Experiment) Dislocation excess in edge dislocation

21.9atoms/nm ⟶ 2.55atoms /(112) plane　　T=520℃(coiling)

Interaction energy between Nb and edge dislocation core: 42.4±0.7 kJ/mol

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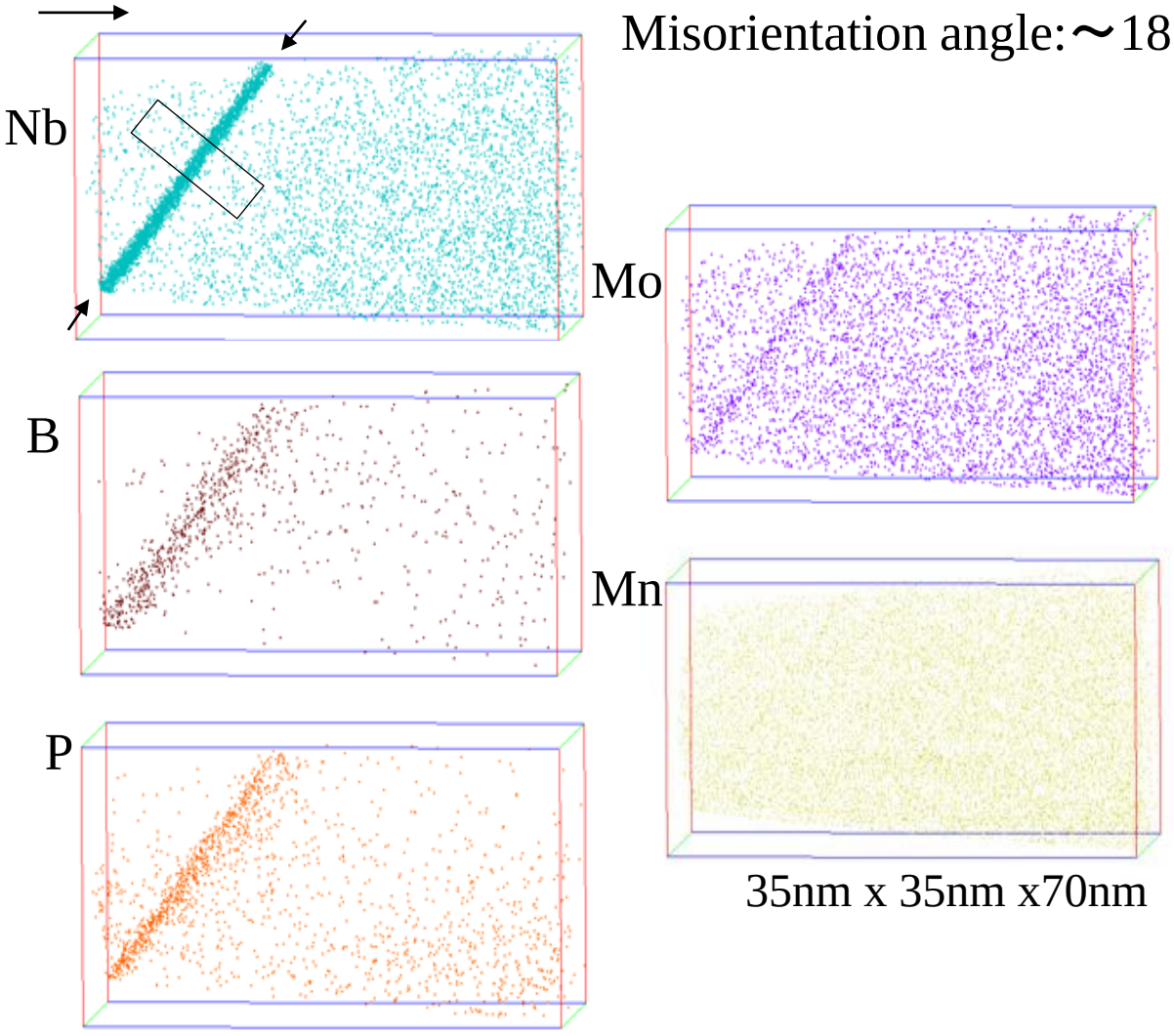
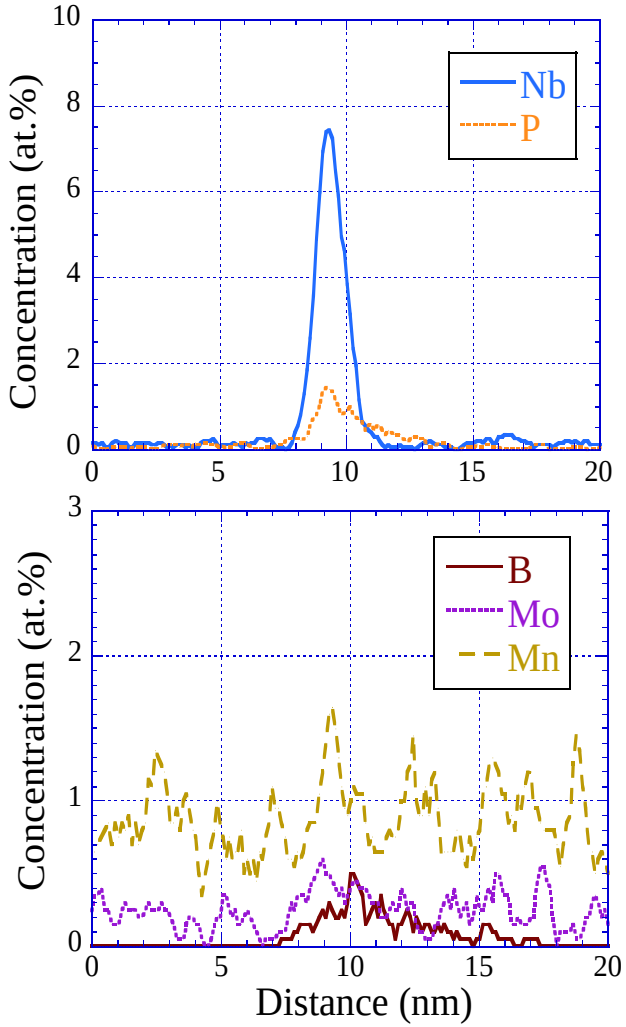
High-angle grain boundary

Misorientation angle:～18°





Planar like heavy segregation of Nb is observed at the grain boundary.
(Maximum concentration : ～8 at.% ）

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Interfacial excess of high-angle GB

Element	Nb	B	P	Mo	Mn
Interfacial excess ($atoms/nm^2$)	9.3 ± 0.30	1.2 ± 0.11	2.9 ± 0.17	0.6 ± 0.08	0.4 ± 0.06

Segregation energy of Nb at high-angle grain boundary

→ 37.1±0.4 kJ/mol (monolayer model)

～almost the same as segregation energy to dislocation

(～42 kJ/mol)

There is a similar tendency of element in the order of segregation degree between the dislocation and the grain boundary.

The two interactions of Nb atoms with dislocation and grain boundary are caused by the same mechanism, namely, “size effect”.

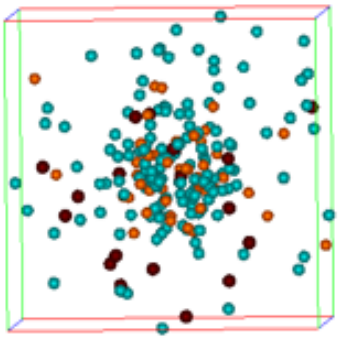
Size of substitutional solute element:

B < P < Fe ~ Mn < Cr < Ti < Mo < Nb

First-principles calculation by Olsson *et al.*(2010), Anda(2012)

Segregation sites

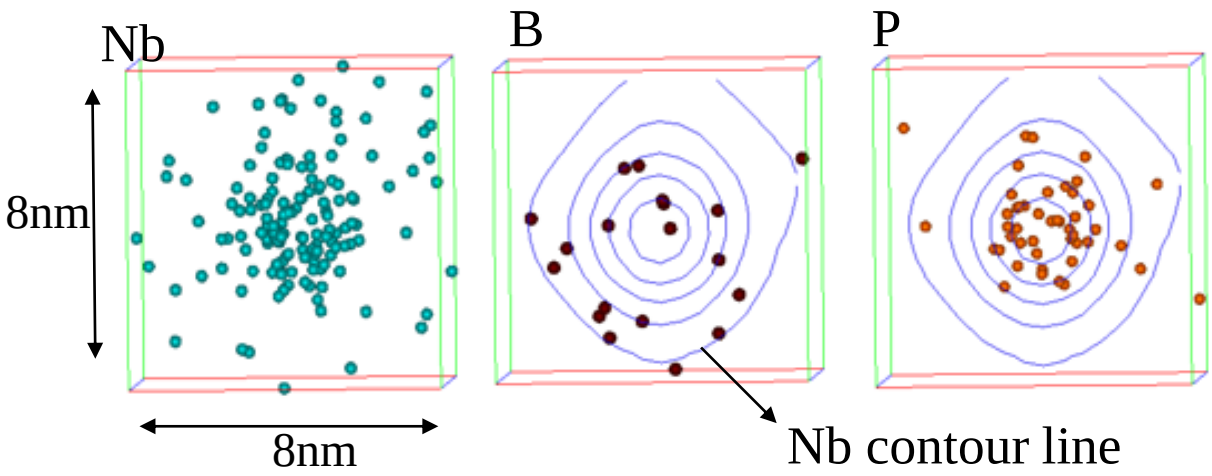
8nm x 8nm x 10nm

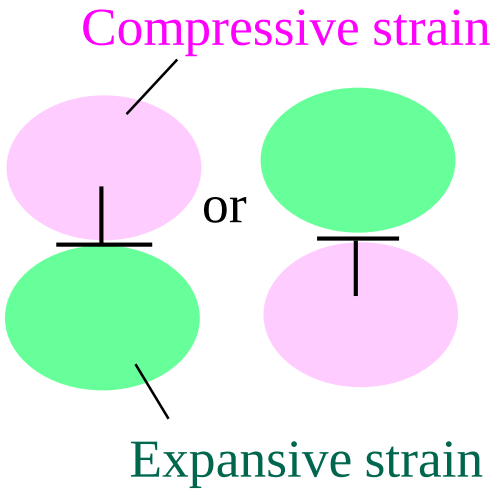


(Size)

Nb > Fe → Expansive strain region

B, P < Fe → Compressive strain region





No distinct difference in the center position of atomic distribution was observed among these elements .

<Possibilities>

B segregates in the expansive strain region as interstitial atoms.

P has an attractive interaction with Nb, or P prefers a disordered structure chemically.

Conclusion

1) We revealed the presence of "Nb-Cottrell atmosphere" for the first time using atom probe tomography.

2) The segregation energy of Nb to edge dislocation core was estimated to be 42.4±0.7 kJ/mol, which was almost the same as the grain boundary segregation energy.

3) The large attractive interaction between Nb and dislocation was due to its large atomic size (→ size effect).

The large interaction of Nb-dislocation causes the retardation of the recovery of dislocations at high temperatures.

J. Takahashi, K. Kawakami, J. Hamada*, K. Kimura: Acta Mater. 107 (2016) 415.