Current status of structural materials

Self healing material

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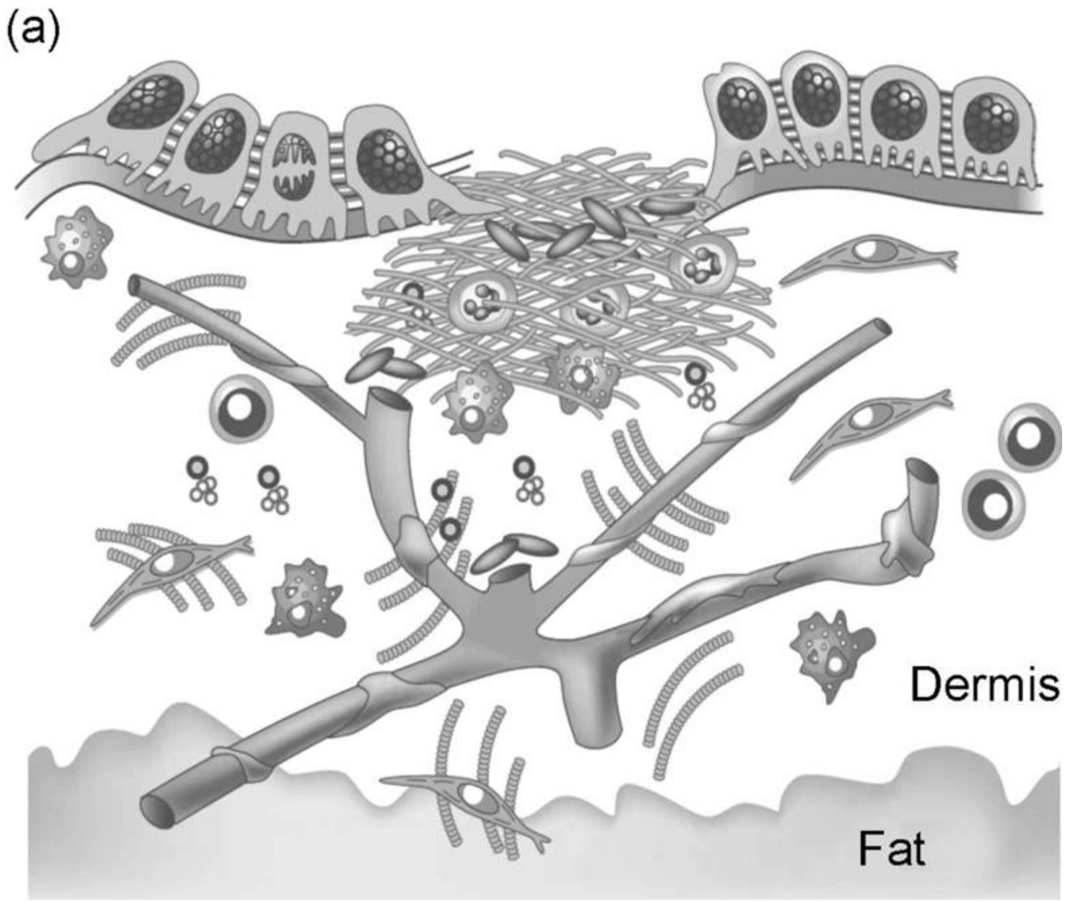
목차

1. Concept of Self healing material



Human skin

The ability of a material to heal(recover/repair) damages automatically and autonomously without any external intervention

Damage prevention principle ⟶ **Damage management principle**

(1) Extrinsic   Microcapsule embedment

Correspondence and requests for materials should be addressed to D.J.W. (e-mail: david.wineland@boulder.nist.gov).

Autonomic healing of polymer composites

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Structural polymers are susceptible to damage in the form of cracks, which form deep within the structure where detection is difficult and repair is almost impossible. Cracking leads to mechanical degradation[1–3] of fibre-reinforced polymer composites; in microelectronic polymeric components it can also lead to electrical failure[4]. Microcracking induced by thermal and mechanical fatigue is also a long-standing problem in polymer adhesives[5]. Regardless of the application, once cracks have formed within polymeric materials, the integrity of the structure is significantly compromised. Experiments exploring the concept of self-repair have been previously reported[6–8], but the only successful crack-healing methods that have been reported so far

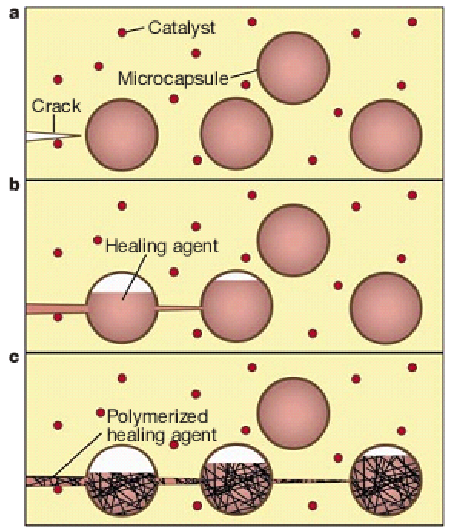
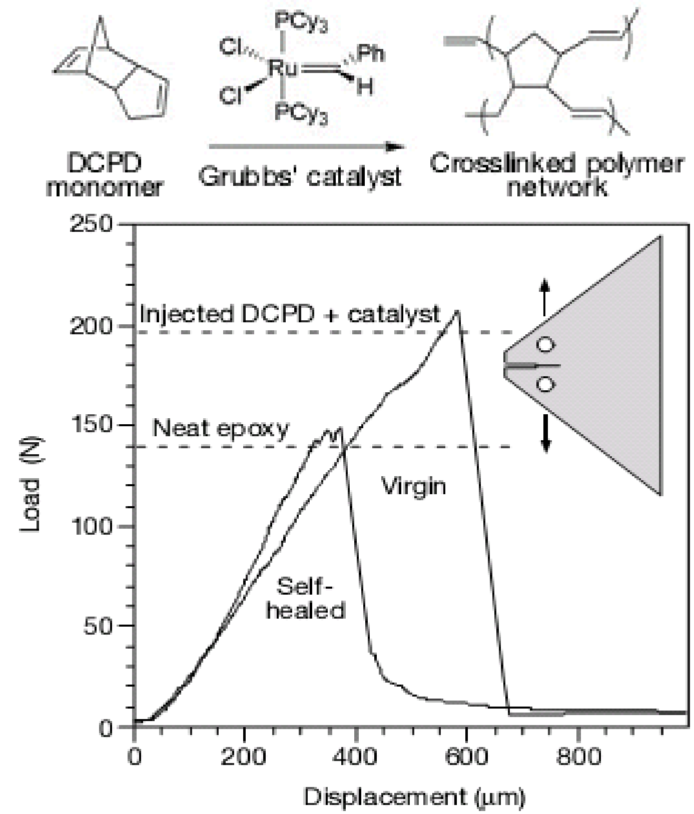


Figure 1 The autonomic healing concept. A microencapsulated healing agent is embedded in a structural composite matrix containing a catalyst capable of polymerizing the healing agent. **a**, Cracks form in the matrix wherever damage occurs; **b**, the crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action; **c**, the healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed.

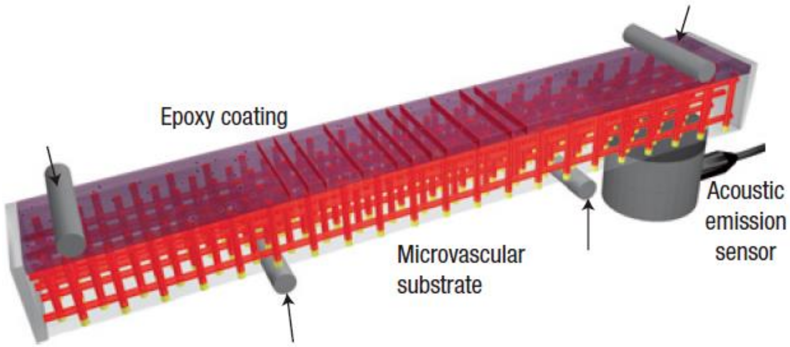


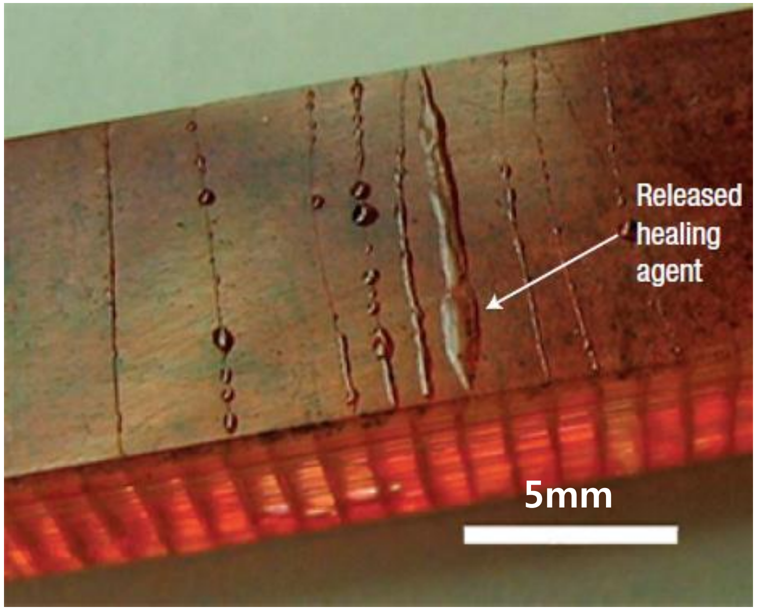
White et al., Nature, 409, 794-797 (2001).

Microcapsulation of Epoxy monomer

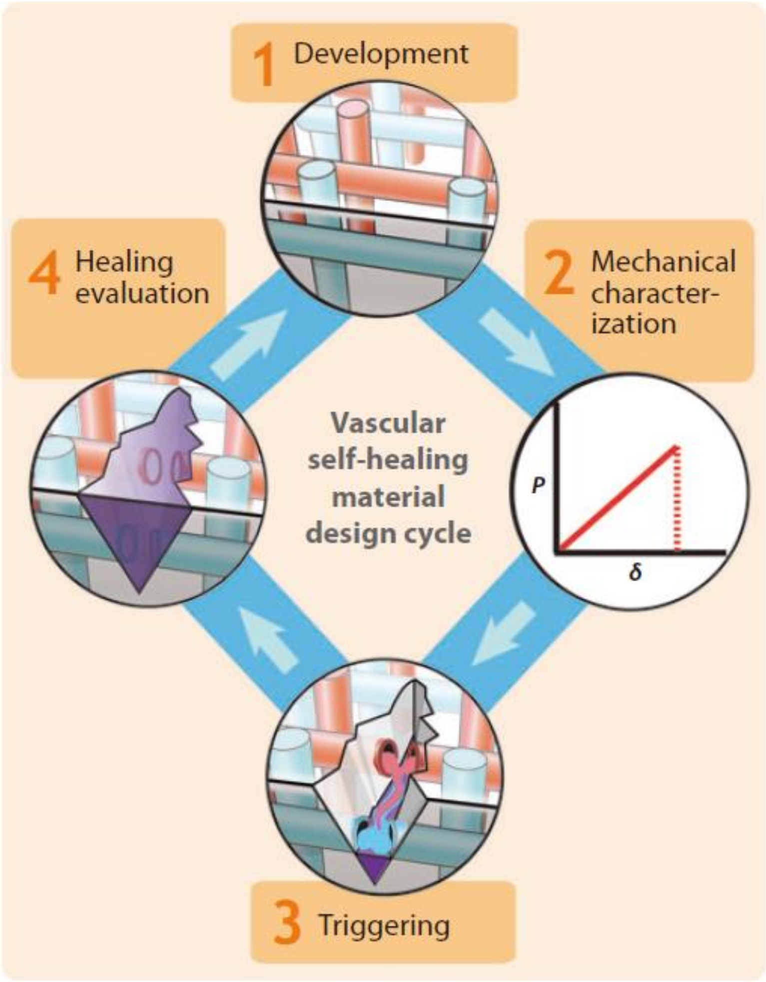
→ **Polymerization of monomers**

(1) Extrinsic   Vascular system





KATHLEEN S. TOOHEY, Nature materials. Vol.6, (2007)



B.J. Blaiszik, Annu.Rev.Mater.Res. (2010)

Epoxy can flow through the vascular system → Multiple healing effect

2. Self healing polymer material

(1) Extrinsic   Vascular system

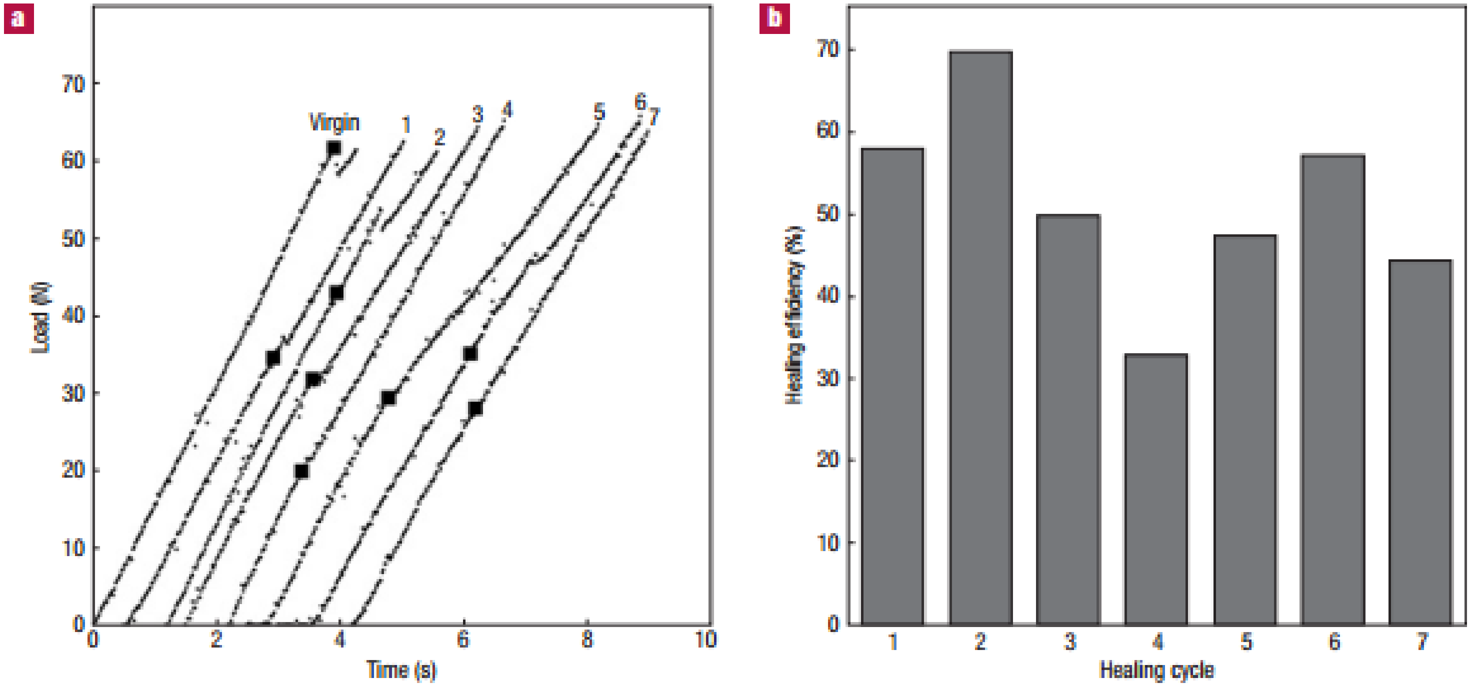


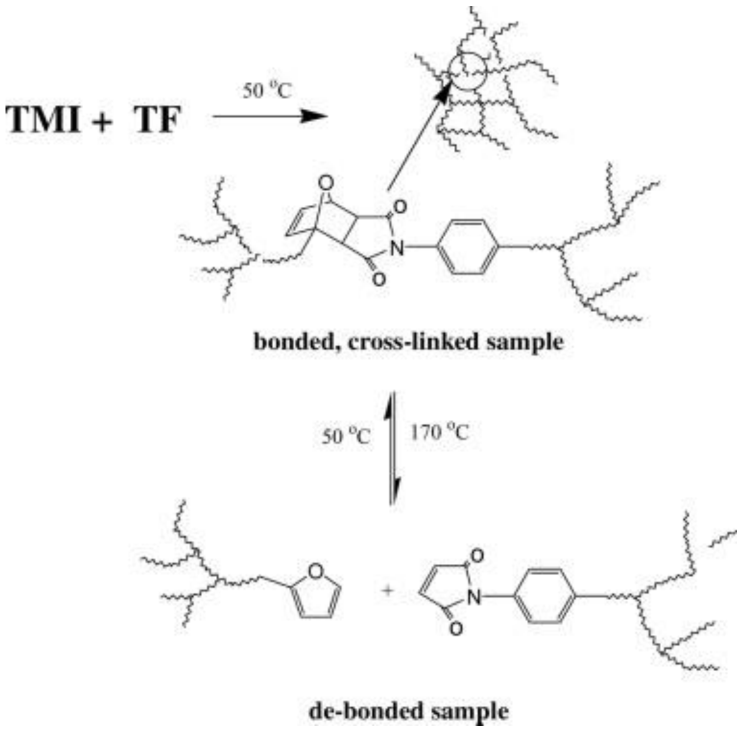
Figure 2 Mechanical behaviour and healing efficiency. a, Load data for the virgin- and healed-specimen tests (1–7) for the best specimen, where the large squares denote the critical crack event for each. Loading traces were shifted 200–500 ms to visualize each data set individually. **b,** Healing efficiency for each successive loading of this coated microvascular beam (10 wt% catalyst in the coating).

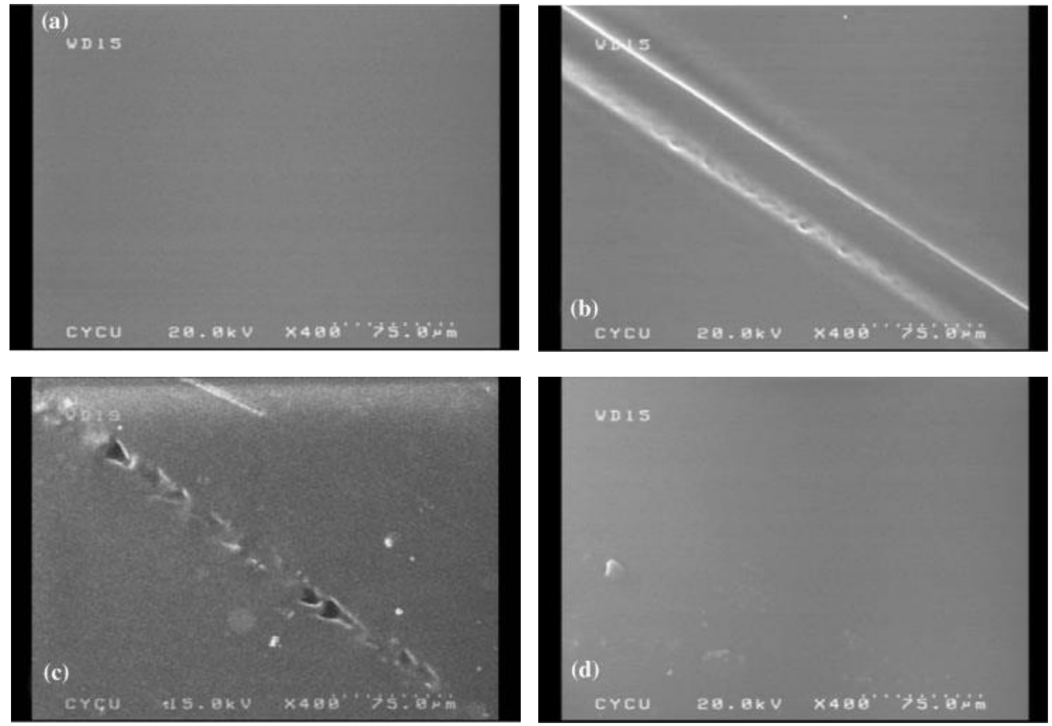
KATHLEEN S. TOOHEY, Nature materials. Vol.6, (2007)

Epoxy can flow through the vascular system ⟶ Multiple healing effect

2. Self healing polymer material

(2) Intrinsic   Diels-Alder reaction





- Thermally reversible crosslinking reaction of TMI and TF through DA and retro-DA reactions.

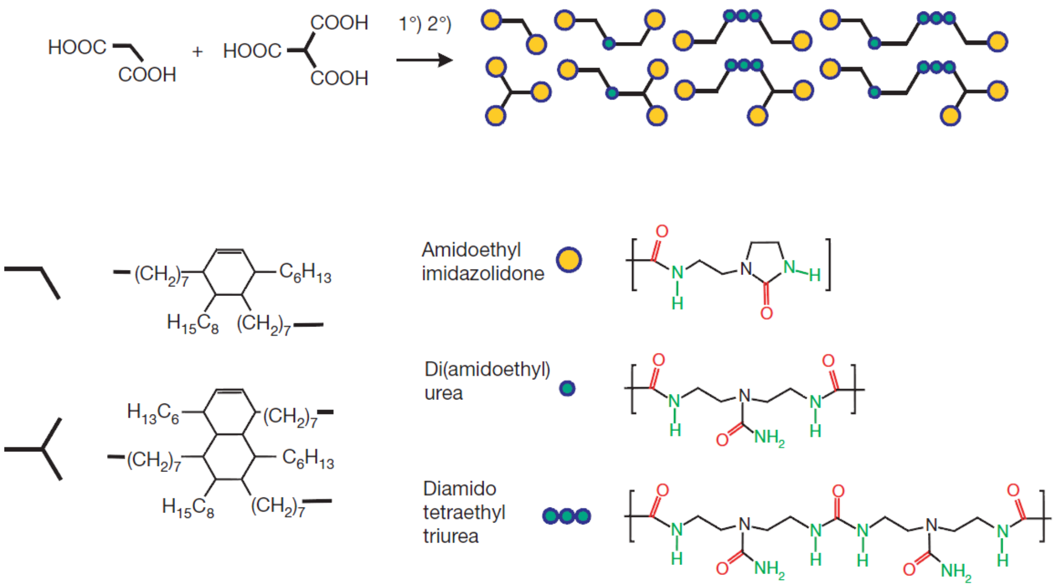
- Test of remendablility. SEM micrographs of
  (a) pristine crosslinked adducts
  (b) knife-cutting sample
  (c) thermally self-repaired sample (50 8C; 12 h)
  (d) thermally self-repaired sample (50 8C; 24 h)

YING-LING LIU, Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 44, 905–913 (2006)

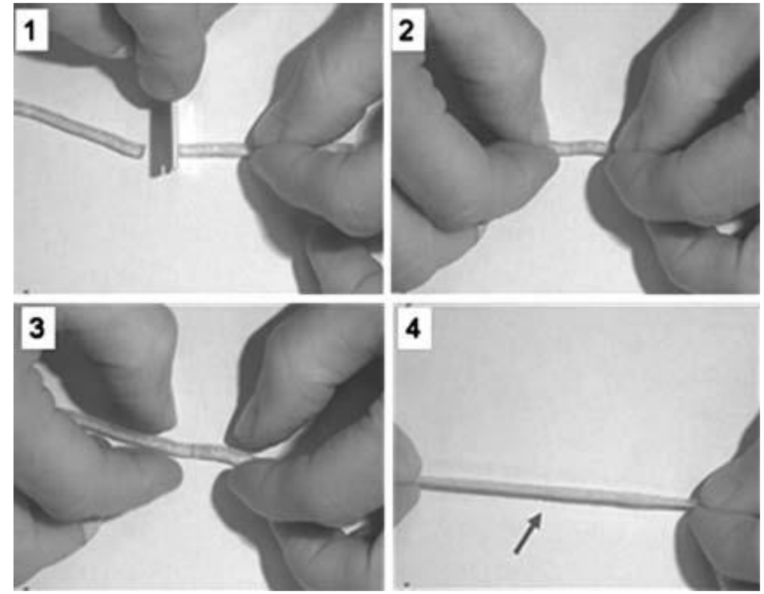
Intrisic self healing reaction through Diels-Alder reaction

2. Self healing polymer material

(2) Intrinsic Supramolecular-Hydrogen bonding



Philippe Cordier1, nature, Vol.451, 21 (2008)

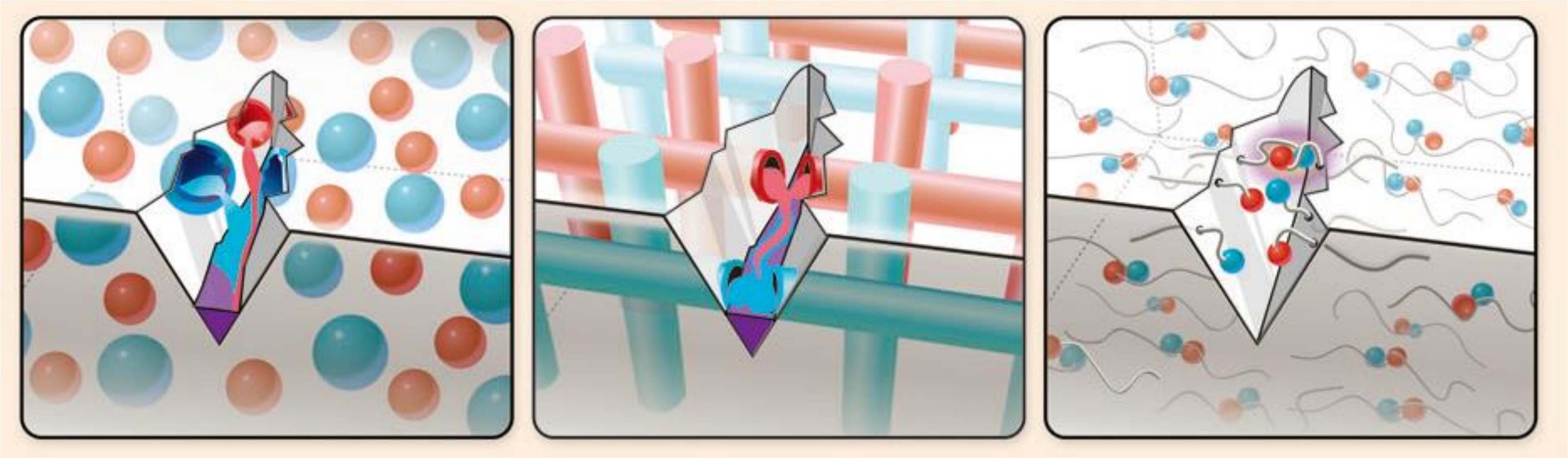


Self-healing polymers by gently pressing them towards each other for few minutes at room temperature.

Intrinsic self healing effect through hydrogen bonding

2. Self healing polymer material

B.J.Blaiszik, et al., Annu.Rev.Mater.Res. vol40, 2010



Microcapsule embedment | Vascular system | Intrinsic

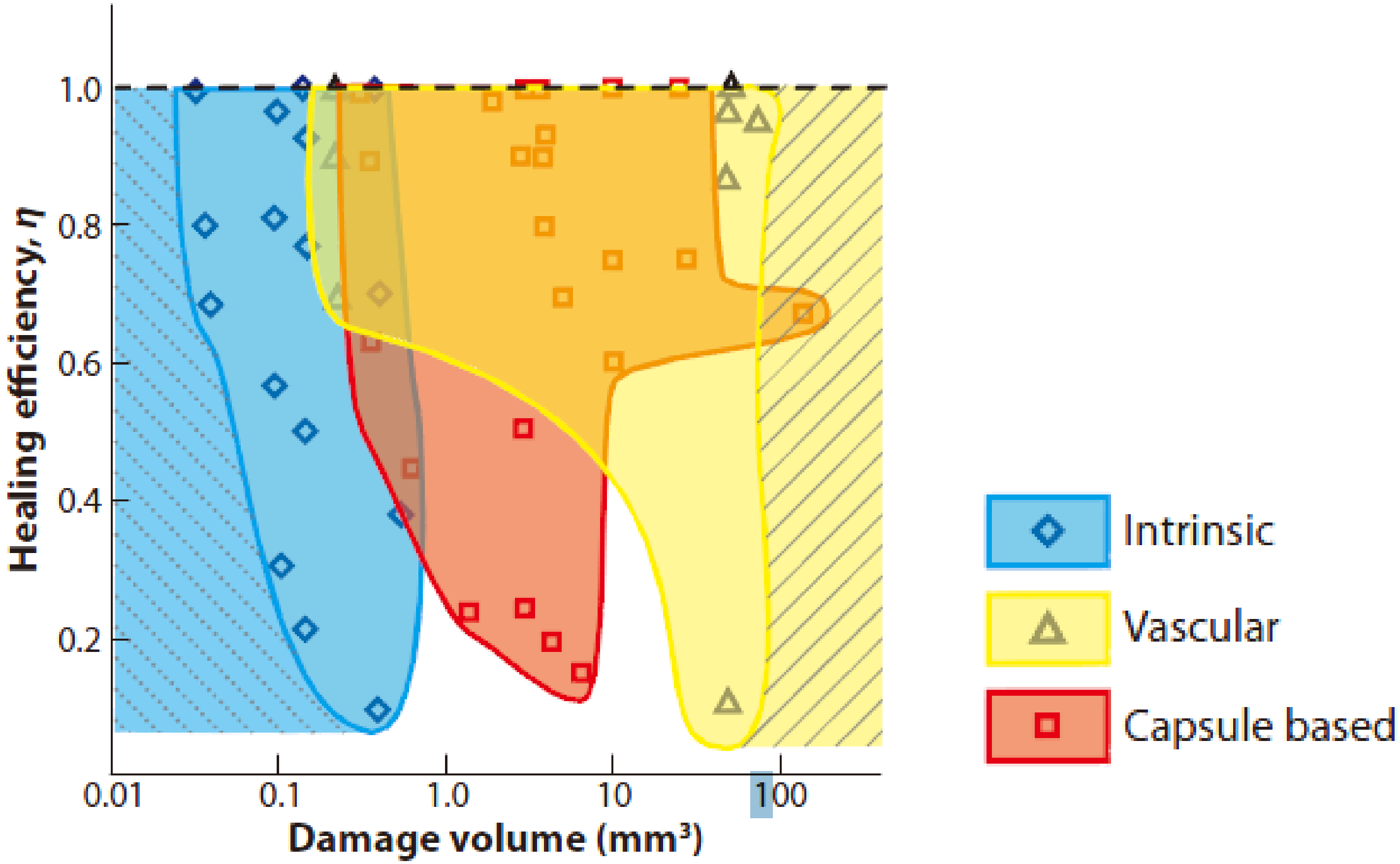
2. Self healing polymer material

Stocking

Coating

Case

2. Self healing polymer material



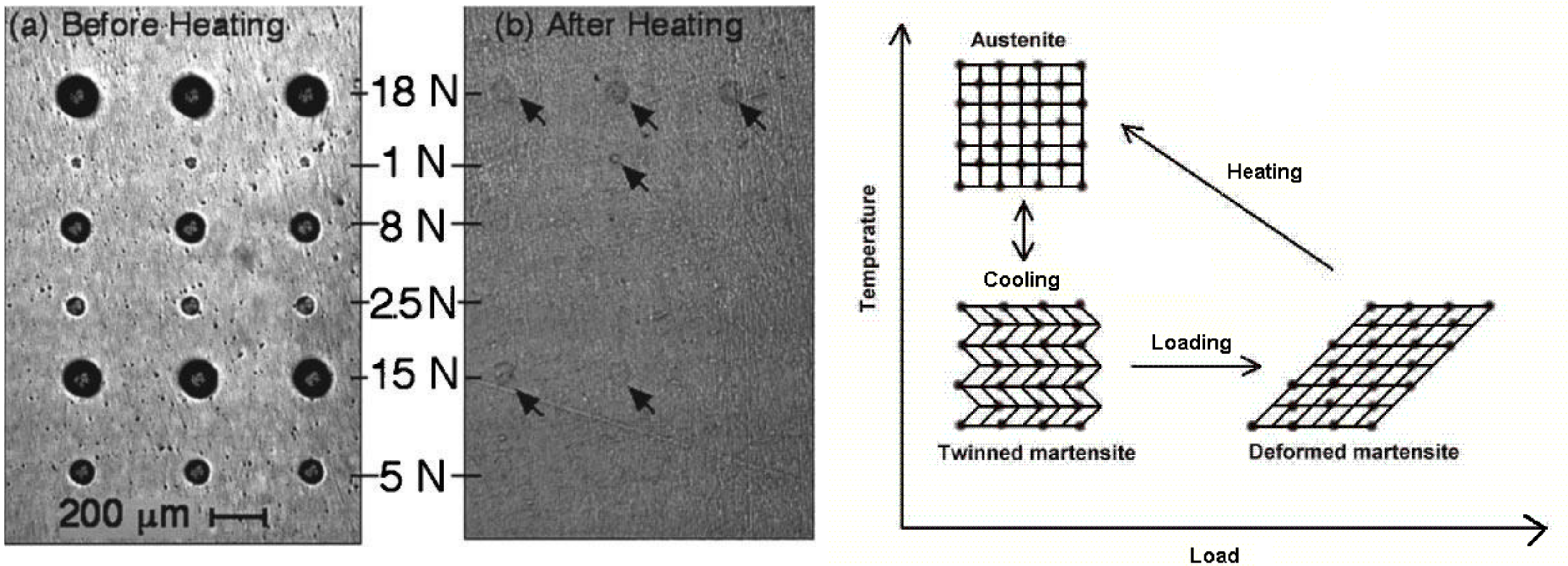
Key issue : How to move healing agent to damaged site?

Ex) Polymer : Application of appropriate healing mechanism considering damaged volume

3. Self healing metallic material

(1) Diffusionless transformation

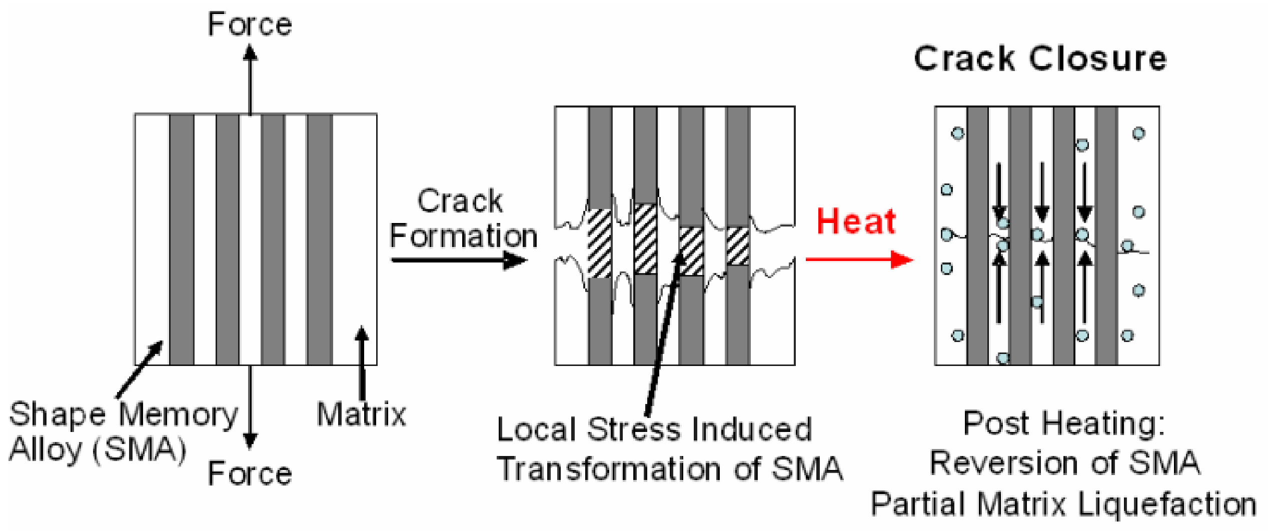
Shape memory alloy



Self healing effect through shape memory effect

3. Self healing metallic material

(1) Diffusionless transformation **Shape memory alloy reinforcement – Sn-13wt%Bi**

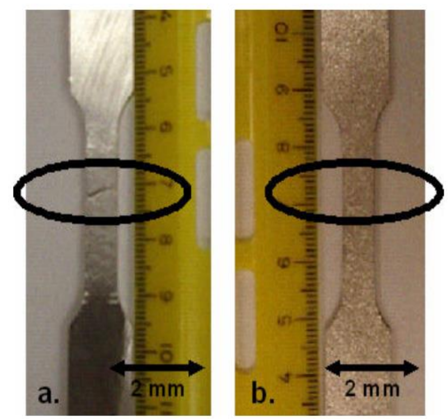


NiTi wire : 190.5㎛, 1% volume fraction, martensite, As:88°C, Af:105°C

Healing : 169℃, 24h

↳ reverse martensitic transformation

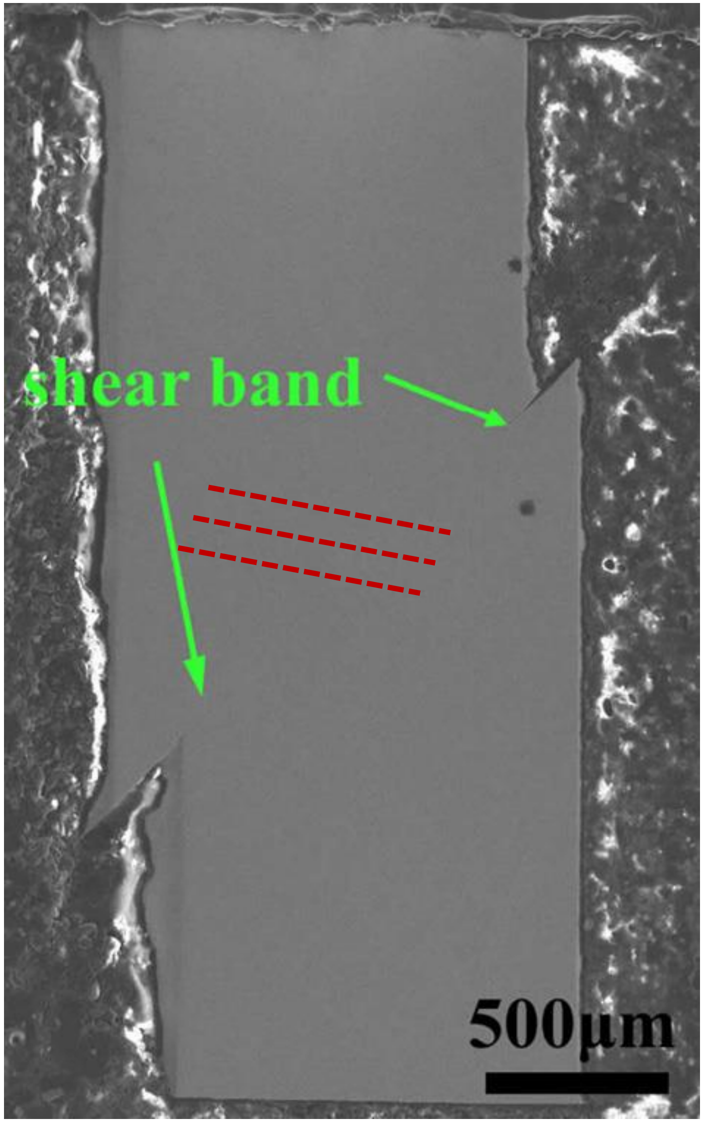
↳ partial melting of matrix(15~20%)

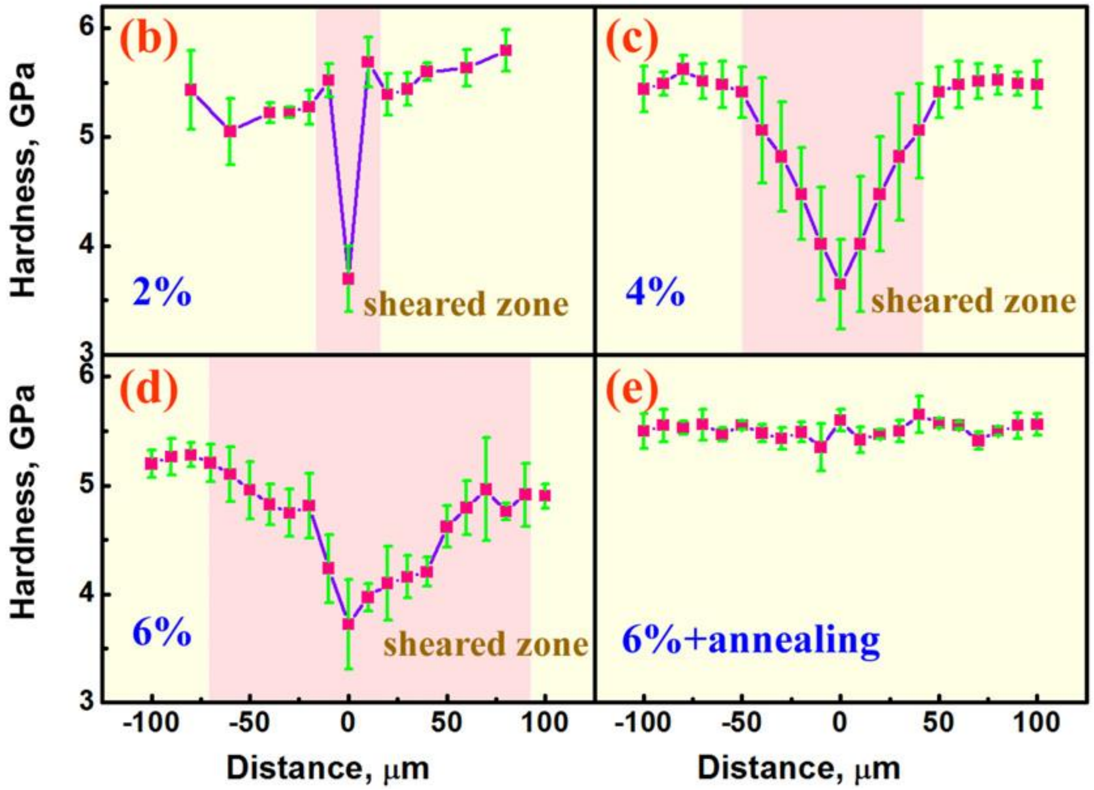


Shape memory effect + Viscous flow of liquid metal

(2) Relaxation

Metallic glass

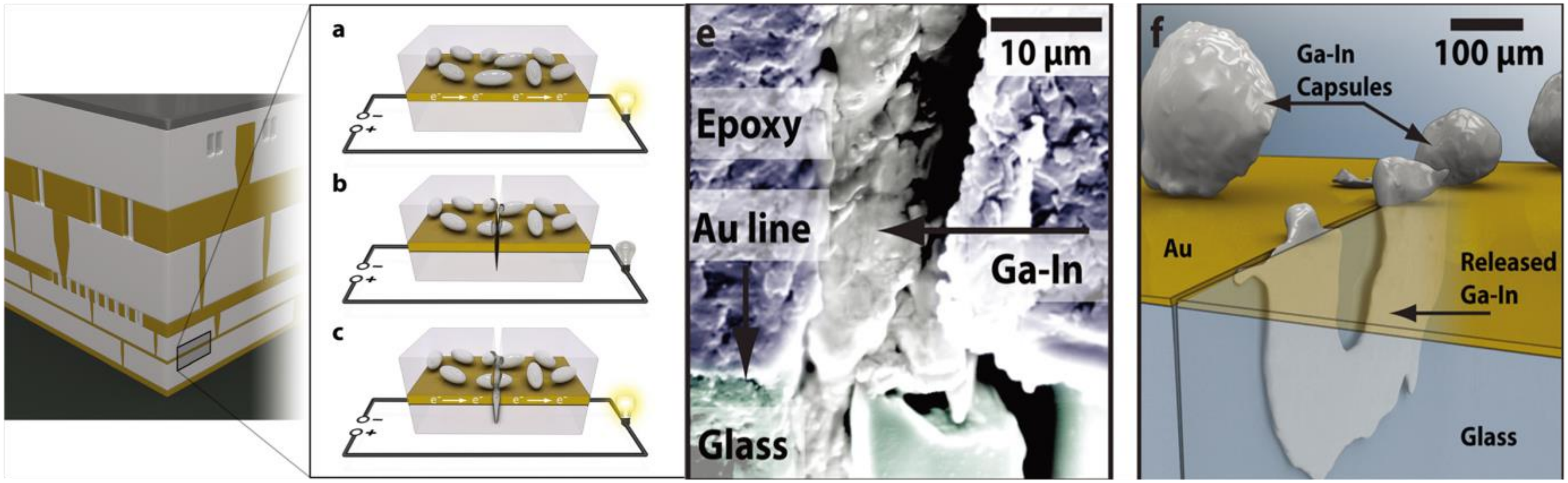




Free volume occurs

⟶ **Relaxation : Recovery of hardness**

(3) Viscous flow of liquid **Microencapsulation**



B.J. Blaiszik, Adv.Mater. 2012, 24, 398-401

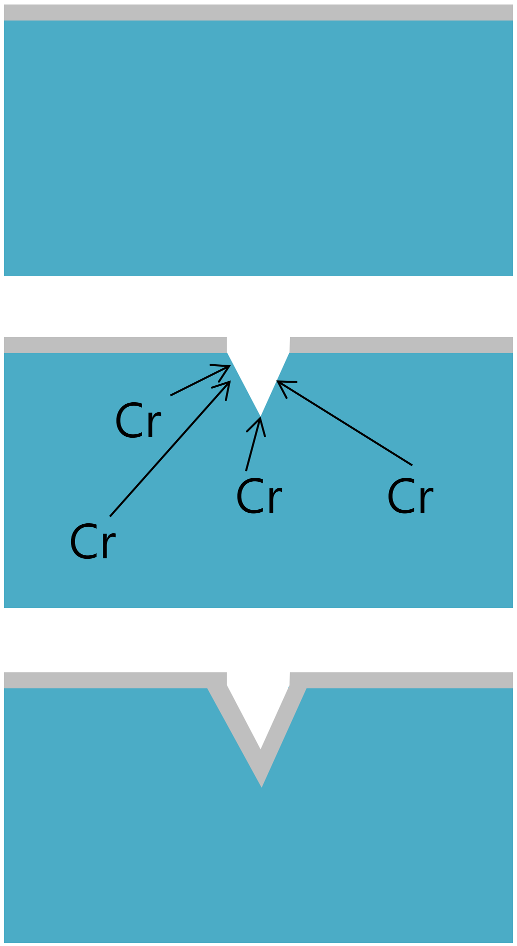
A crack occurred after 4 point bend test

⟶ The crack was repaired by Ga-In liquid inside the microcapsule

⟶ Recovery of 99% electroconductivity with just 20us

(4) Diffusion

Stainless steel



Crack occur →

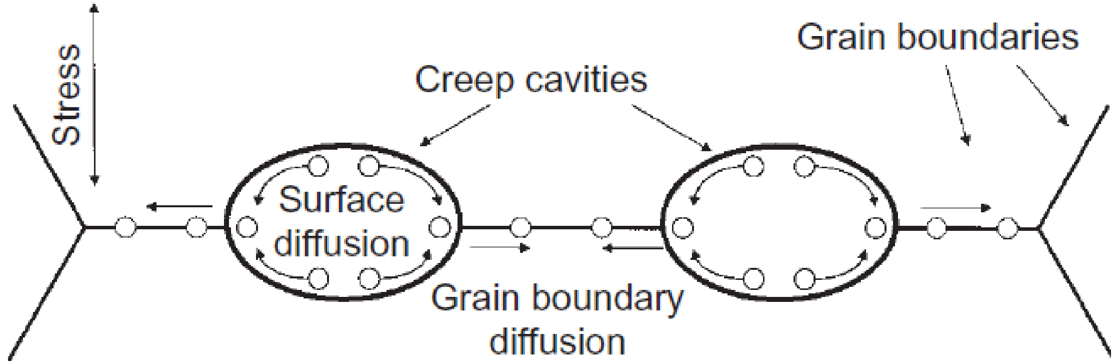
Chrome atoms diffuse to surface and become oxidation.

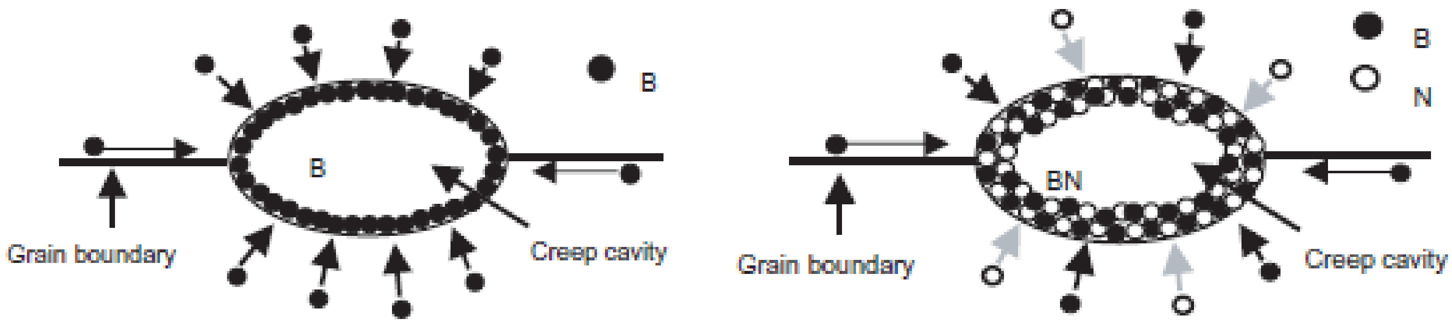
→ New protective layer

Material	Damage	Condition of self healing	Driving force of self healing
Stainless steel	Scratch, Crack	Existence of Oxygen molecules near the surface	Oxidation of solute Chrome atoms

(4) Diffusion

B, BN segregation at 304 steel





(b) B segregation (MP : 2080°C)

(c) BN precipitation (MP : 3000°C)

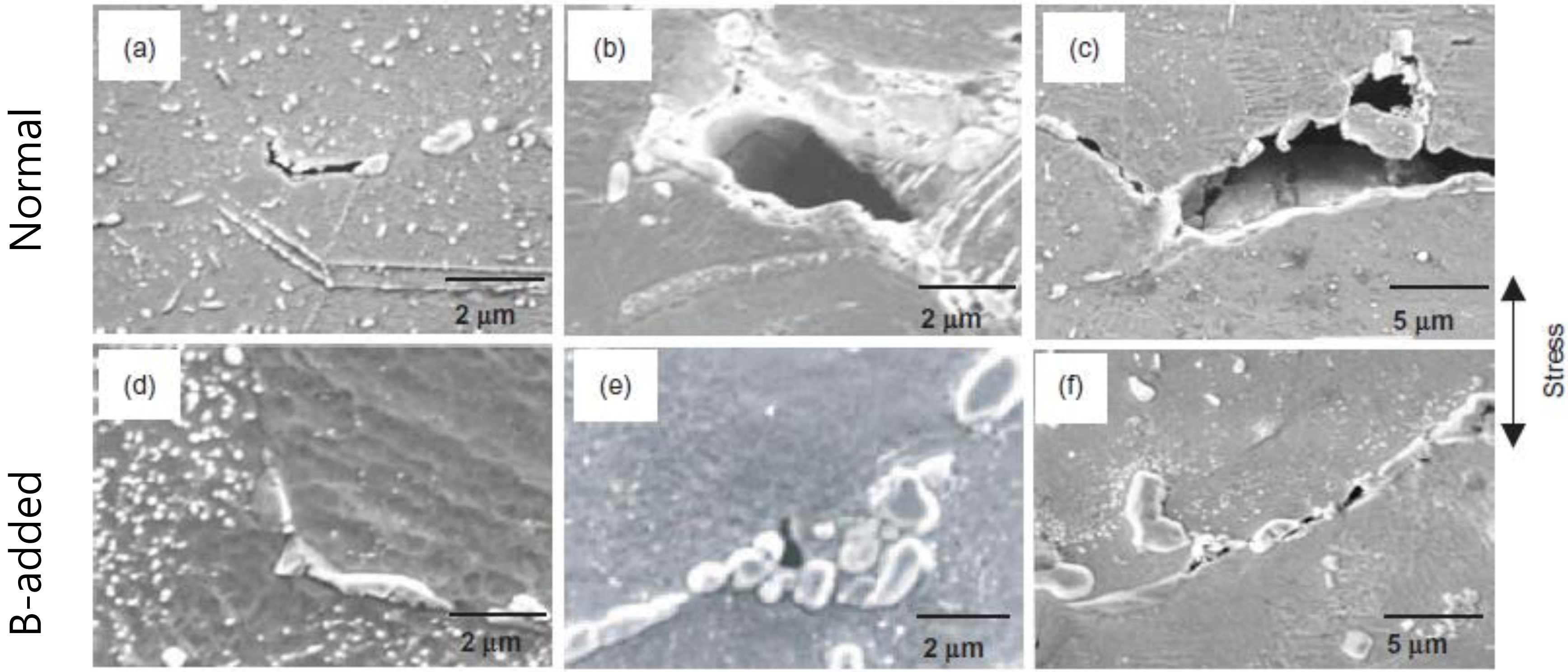
B, BN : high melting temperature(mp:2080°C,3000°C)

➡ **Suprresing the creep cavity surface diffusion of 304 steel**

3. Self healing metallic material

(4) Diffusion

B, BN segregation at 304 steel



(a) t=238h(t/tr=0.71), (b) t=289h(t/tr=0.87), (c) tr=333h, (d) t=8,150h(t/tr=0.68), (e) t=10,200h(t/tr=0.86), (f) tr=11,900h.
t: creep time. tr: rupture time.

How to increase diffusivity?

4. Diffusivity

(1) Pipe diffusion Al-8Zn-2.5Mg-1Cu

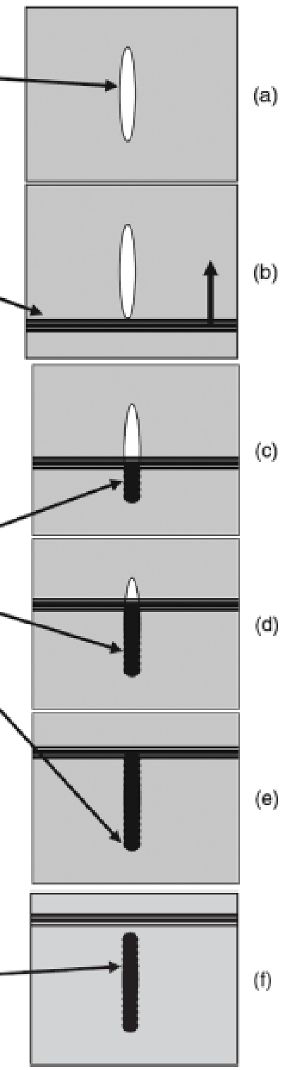
→ Faster than Volume diffusion grain boundary diffusion (100,000~1000,000)

Short fatigue crack initiation

Subsequent dislocation moving across crack region

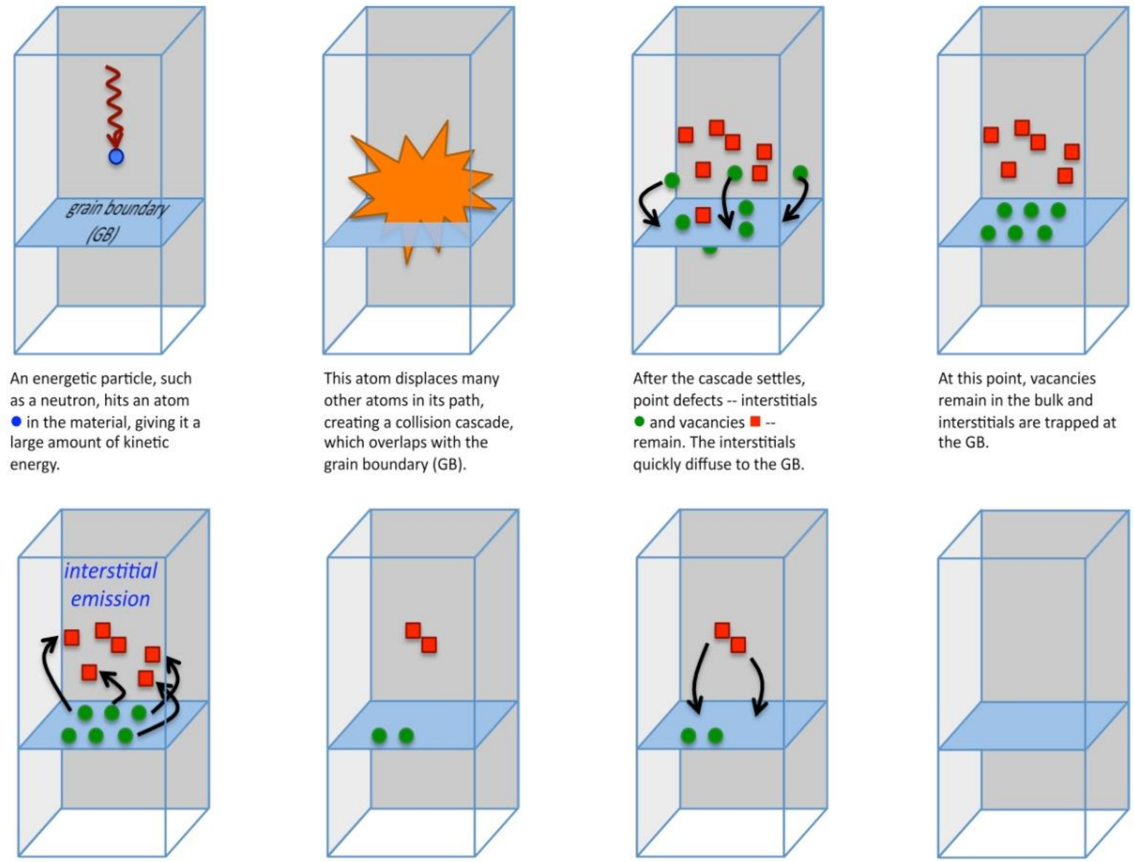
Solute present on saturated dislocation deposits into the former crack region as precipitate

Precipitate forms by dynamic precipitation closing crack and providing localized strengthening



Porosity closure was studied in Al powder alloys (Al-8Zn-2.5Mg-1Cu)

(2) Nanocrystalline material **Irradiation damage**



An energetic particle, such as a neutron, hits an atom ● in the material, giving it a large amount of kinetic energy.

This atom displaces many other atoms in its path, creating a collision cascade, which overlaps with the grain boundary (GB).

After the cascade settles, point defects -- interstitials ● and vacancies ■ -- remain. The interstitials quickly diffuse to the GB.

At this point, vacancies remain in the bulk and interstitials are trapped at the GB.

Surprisingly, these trapped interstitials can re-emit from the GB into the bulk, annihilating the vacancies on time scales much faster than vacancy diffusion.

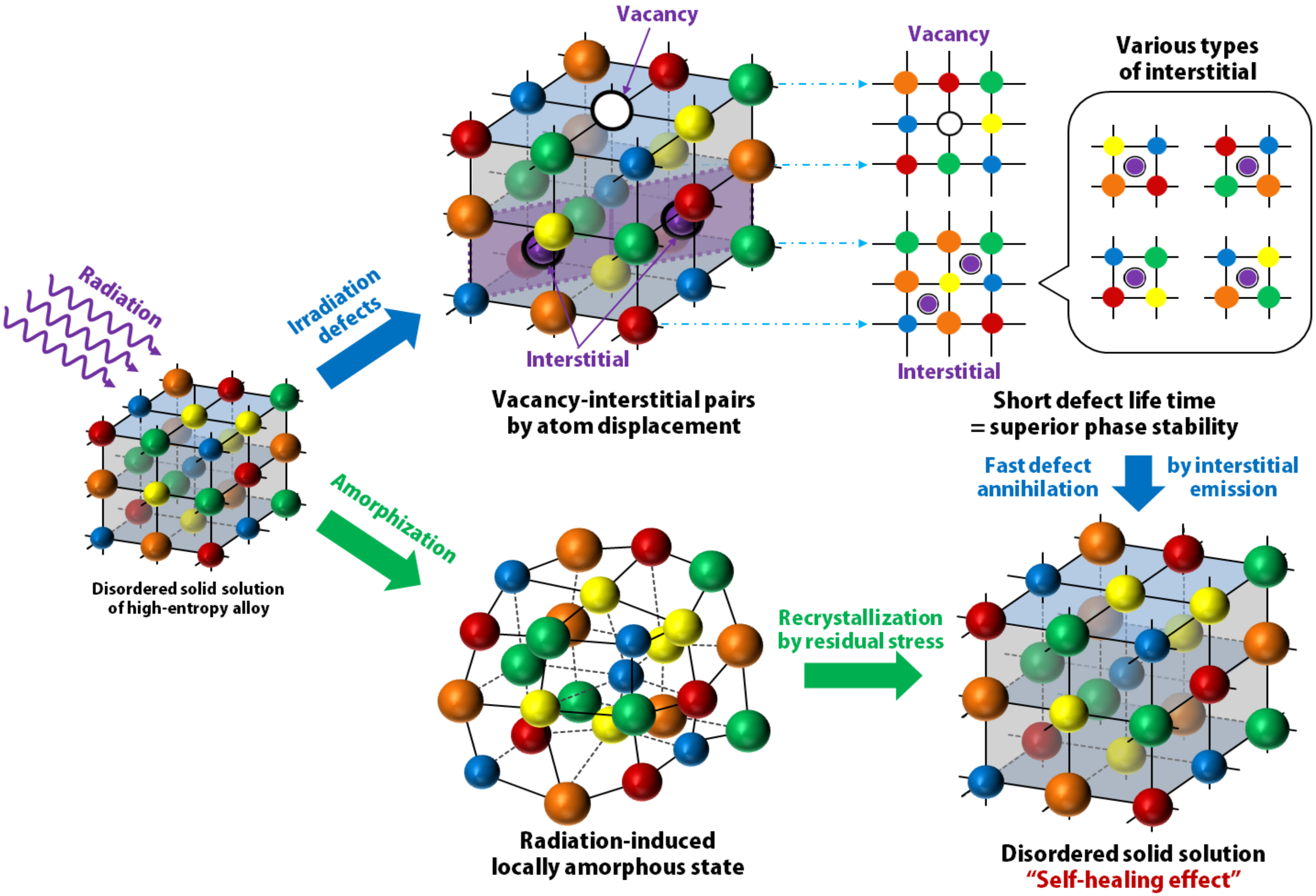
After the interstitial emission events have occurred, some vacancies that were out of reach persist. The system is now in a relatively static situation.

On much longer time scales, the remaining vacancies can diffuse to the GB, completing the healing of the material. At low temperatures this diffusion is exceedingly slow.

In the ideal case, the system returns to a pristine GB. At low temperatures, the only hope for reaching such a state is via the newly discovered interstitial emission mechanism.

Activation energy : Interstitial emission(0.17eV) < Initial of Interstitial(1.6eV)

5. Self healing high entropy alloy



- Vacancy-interstitial : Nanocrystalline effect
- Reversible amorphisation (due to high lattice distortion effect)
- Thermodynamical self healing effect

Thank you for your kind attention