2016 fall <Freshman Seminar>

“New materials to open the future”

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“ Self-healing Material ”

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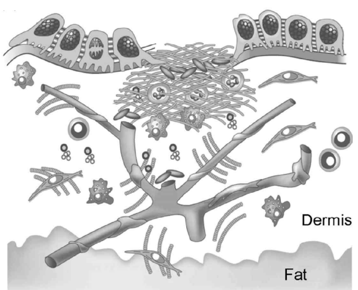
1. Concept of Self-healing material



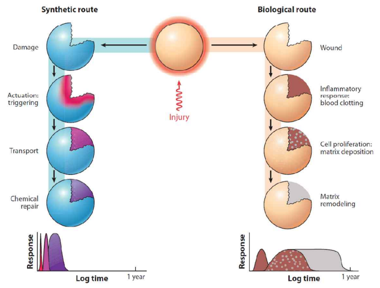
Human skin

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

Damage prevention principle ⟶ Damage management principle

What is self-healing material?

Wound healing vs self healing process *B.J.Blaiszik, et al., Annu.Rev.Mater.Res., vol.40 (2010)*



- **Self healing materials are biomimetic materials that imitate healing process of the organism.**
- **“Self healing” means the ability of a material to heal(recover/repair) damages automatically and autonomously without any external intervention.**

Classification of Self-healing Material

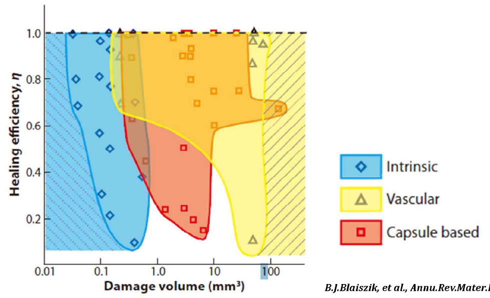
Underlying principle

All self-healing mechanisms require the generation of a mobile phase that can close the crack.

- Type of Trigger
  - Non-Autonomic: Require a small energy input
  - Autonomic: Use the damage it self as the stimulus for healing
- Type of Mobile Phase
  - Extrinsic: Have a sourced mobile phase like microcapsules
  - Intrinsic: Moblie phase themselves

What is self-healing material?

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



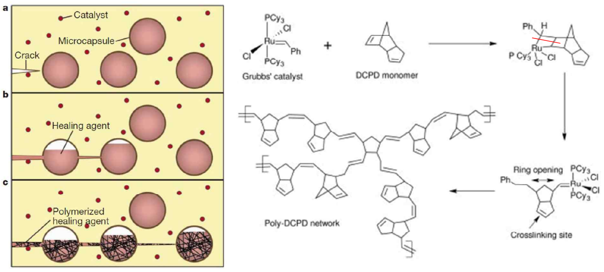
B.J.Blaiszik, et al., Annu.Rev.Mater.Res., vol.40 (2010)

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

4 major component of self-healing process

First reported self healing material : Self healing polymer

S.R.White et al., Nature, Vol.409 (2001)



1. Damage
: Crack

2. Actuation
: Break of microcapsule

3. Transport of healing agent
: Flow into the crack

4. Repairing (Driving force)
: Polymerization

2. Self-healing polymer material

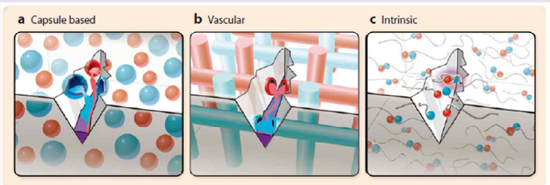


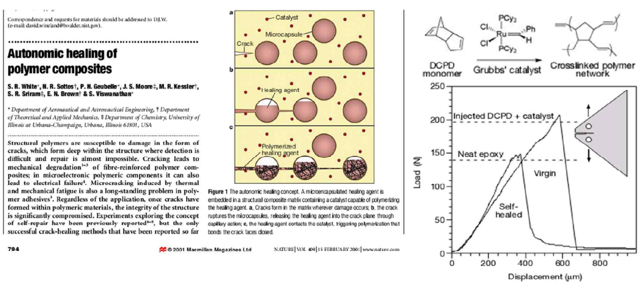
Figure 2
Approaches to self-healing include (a) capsule-based, (b) vascular, and (c) intrinsic methods. Each approach differs according to the method by which healing functionality is integrated into the bulk material. (a) In capsule-based self-healing materials, the healing agent is stored in capsules until they are ruptured by damage or dissolved. (b) For vascular materials, the healing agent is stored in hollow channels or fibers until damage ruptures the vasculature and releases the healing agent. (c) Intrinsic materials contain a latent functionality that triggers self-healing of damage via thermally reversible reactions, hydrogen bonding, ionomeric arrangements, or molecular diffusion and entanglement. Shades of red and blue are used in this figure and throughout the review to show a generalized interaction (purple) between two or more species.

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

2. Self-healing polymer material

(a) Capsule based

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

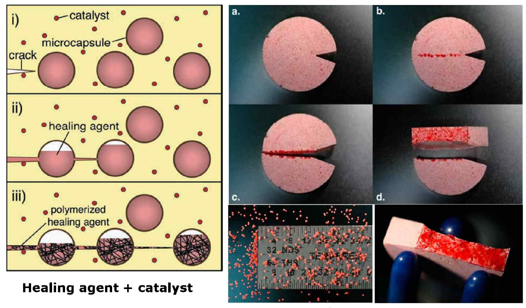


Microcapsulation of Epoxy monomer

⟶ Polymerization of monomers

2. Self-healing polymer material

(a) Capsule based



Healing agent + catalyst

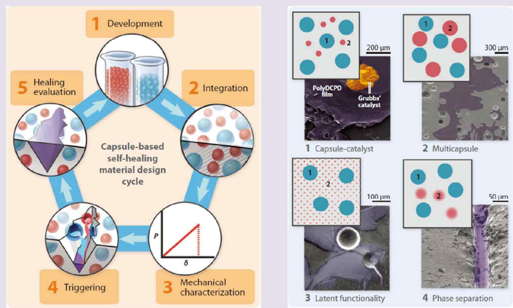
•White et al, 409, Nature, 794-797, 2001

Microcapsulation of Epoxy monomer

⟶ Polymerization of monomers

2. Self-healing polymer material

(a) Capsule based

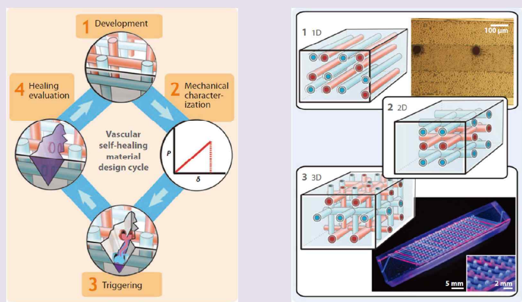


▶ Capsule-based self-healing materials. (a) Capsule-based self-healing includes four main sequestration schemes. (b) The design cycle for capsule-based self-healing materials.

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

2. Self-healing polymer material

(b) Vascular

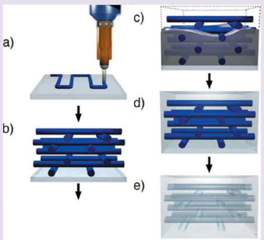


▶ Vascular self-healing materials. (a) Vascular self-healing is organized according to the connectivity of the vascular network. (b) The design cycle for vascular self-healing materials.

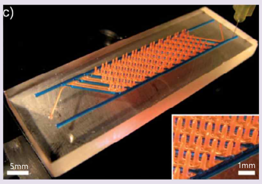
B.J. Blaiszik, Annu.Rev.Mater.Res. (2010)

2. Self-healing polymer material

(b) Vascular



Scheme 1. Schematic representation of the fabrication procedure for 3D microvascular networks by direct-write assembly: a) deposition of fugitive ink (in blue) through cylindrical nozzle; b) multilayer scaffold after ink deposition; c) resin infiltration into scaffold; d) resin solidification to form structural matrix; and e) 3D microvascular network created after removal of fugitive ink.

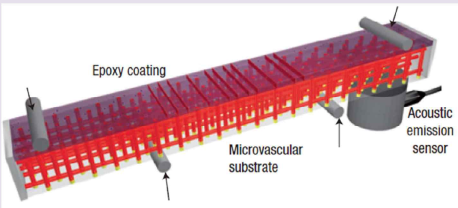


- Microvascular system (Blue : fugitive ink, Orange : wax)
- Ink : paraffin wax, mineral oil, and ferric ferrocyanide nanoparticles(~2.2wt.-%)

Daniel Therriault, Adv. Mater. (2005) KATHLEEN S. TOOHEY, Nature Materials. (2007)

2. Self-healing polymer material

(b) Vascular

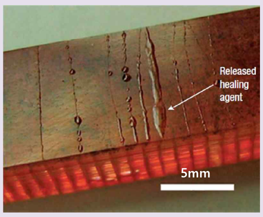


- Schematic diagram of the self-healing structure composed of a microvascular substrate and a brittle epoxy coating containing embedded catalyst in a four-point bending configuration monitored with an acoustic-emission sensor.

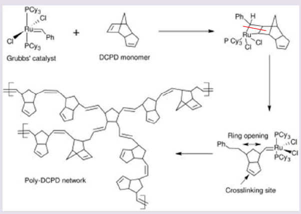
KATHLEEN S. TOOHEY, Nature materials. Vol.6, (2007)

2. Self-healing polymer material

(b) Vascular



- Optical image of self-healing structure after cracks are formed in the coating (with 2.5 wt% catalyst), revealing the presence of excess healing fluid on the coating surface.

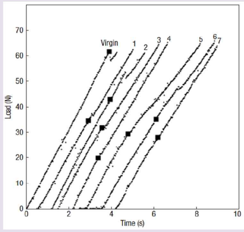


- Ring opening metathesis polymerization of DCPD.

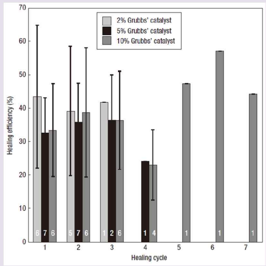
KATHLEEN S. TOOHEY, Nature materials. Vol.6, (2007) Larin G.E., Polymer Engineering and Science, 46, 1804-11. (2006)

2. Self-healing polymer material

(b) Vascular



- 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.



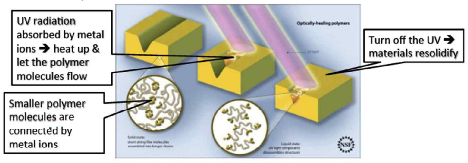
- Grubbs' catalyst effects on healing efficiency.

Epoxy can flow through the vascular system ⟶ Multiple healing effect

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

2. Self-healing polymer material

(c) Intrinsic

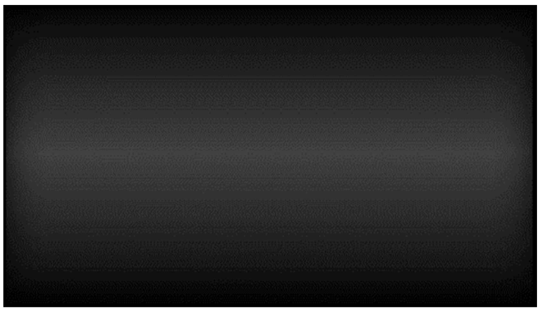


(Source: NSF)

- Metallo-supramolecular polymers
  - ability to liquefy when subjected to UV
  - fill in small dents and scratches
    - -> re-solidify when the light source is turned off.
- Other energy sources can be used instead of UV

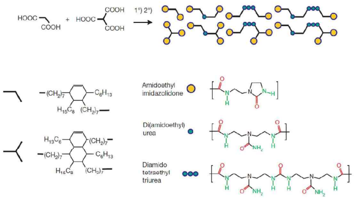
Video : https://www.youtube.com/watch?v=X0cu348ei9g
Video : https://www.youtube.com/watch?v=h-fka0wfY8w
http://news.softpedia.com/news/New-Polymer-Enables-Self-Healing-Car-Paints-196226.shtml

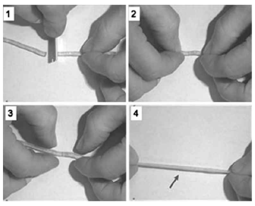
(c) Intrinsic Principle of UV polymer



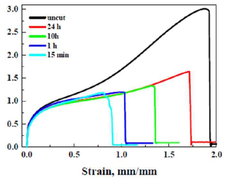
2. Self-healing polymer material

(c) Intrinsic **Supramolecular-Hydrogen bonding**





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

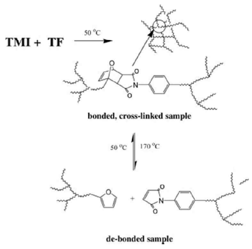


Intrinsic self healing effect through hydrogen bonding

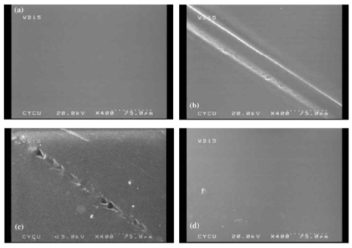
H-bond rebuilt, so material can be recovered without any external stimulus(ex. light, Heat, etc) or additives.

2. Self-healing polymer material

(c) 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)

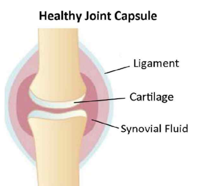
Intrisic self healing reaction through Diels-Alder reaction Movie III

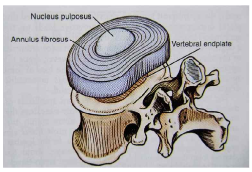
(c) Intrinsic **Example of sticking** Self-healing polymers by gently pressing them towards each other for few minutes at room temperature.

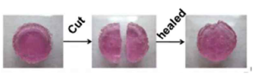
(c) Intrinsic **Car scratch**

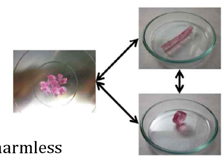
2. Self-healing polymer material

(c) Intrinsic









Injectable and harmless

Pablo Casuso, Ibon Odriozola, et al. Injectable and Self-healing Dynamic Hydrogels Based on Metal(I) Thiolate/Disulfide Exchange as Biomaterials with Tunable Mechanical Properties. *Biomacromolecules*(2015).

2. Self-healing polymer material

(d) Application

Stocking

Coating

Case

Movie IV

2. Self-healing polymer material

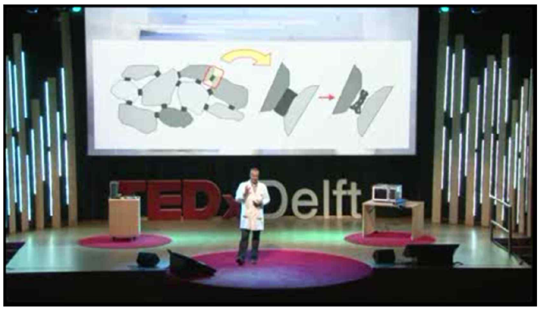
(d) Application

- Military Industry
  - body armor, bulletproof material, etc.
- Structural Material
- Bioengineering
  - artificial organ, artificial skin, artificial blood vessel , etc.
- Space Industry

Movie IV

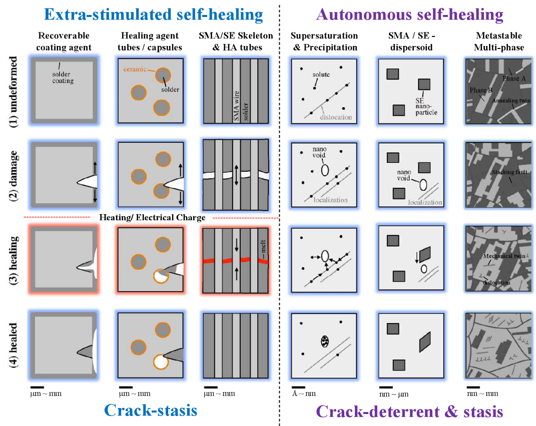
3. Self-healing ceramic material

Concrete



(d) Application

4. Damage-tolerant self-healing metallic material



3. Self-healing ceramic material

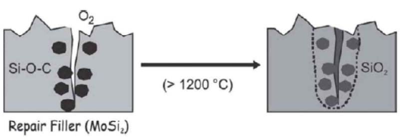


Figure 4. Self-healing of cracks in SiOC/$MoSi_2$ oxidation protection coatings on SiC-ceramics.

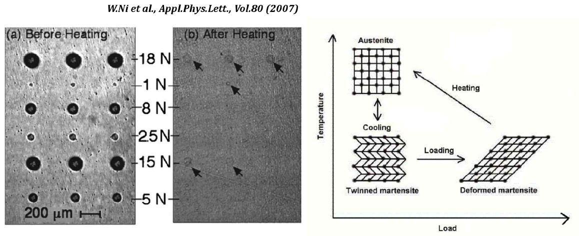
- reactive filler ($MoSi_2$) embedded in a Si-O-C matrix is oxidized by permeating oxygen
  -> SiO_2 is formed and closes the crack completely
- other types of filler and matrixes, material using other types of stimulus are being researched

Videos : https://www.youtube.com/watch?v=0I_9NDZ8VZA
Martin D. Hager et. al., *Self Healing Material*, Advanced Materials, 2010, 22, 5424-5430

4. Damage-tolerant self-healing metallic material

(a) Shape memory alloy(SMA)

W.Ni et al., Appl.Phys.Lett., Vol.80 (2007)



Self healing effect through shape memory effect

1. Damage
: Indent

2. Actuation
: Reverse martensitic transformation of SMA

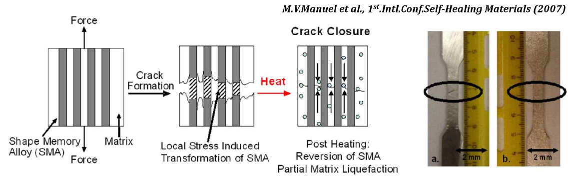
3. Transport of healing agent
: Diffusionless process

4. Repairing (Driving force)
: Heating

4. Damage-tolerant self-healing metallic material

(b) SMA reinforcement Sn-13wt%Bi

M.V.Manuel et al., 1st.Intl.Conf.Self-Healing Materials (2007)



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

Healing : 169℃, 24h

↳ reverse martensitic transformation — Shape memory effect

+

↳ partial melting of matrix(15~20%) — Viscous flow of liquid metal

1. Damage
: Crack

2. Actuation
: Reverse martensitic transformation of SMA

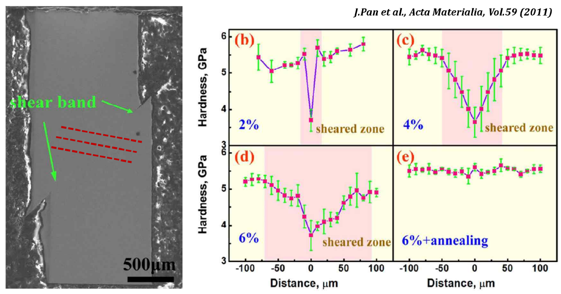
3. Transport of healing agent
: Flow of Melt

4. Repairing (Driving force)
: Heating

4. Damage-tolerant self-healing metallic material

(c) Relaxation of metallic glass : Recovery of hardness

J.Pan et al., Acta Materialia, Vol.59 (2011)



1. Damage
: Shear band

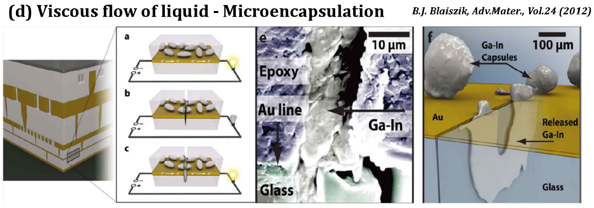
2. Actuation
: Heating

3. Transport of healing agent
: Diffusion (Removing free volume)

4. Repairing (Driving force)
: Relaxation

4. Damage-tolerant self-healing metallic material

(d) Viscous flow of liquid - Microencapsulation *B.J. Blaiszik, Adv.Mater., Vol.24 (2012)*



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

1. Damage
: Crack

2. Actuation
: Break microcapsules

3. Transport of healing agent
: Flow into crack

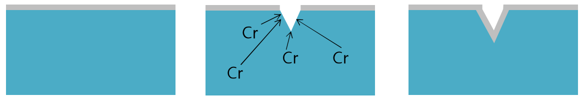
4. Repairing (Driving force)
: Fill the crack

4. Damage-tolerant self-healing metallic material

(e) Stainless steel : Passive oxide layer

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

1. Damage
: Crack

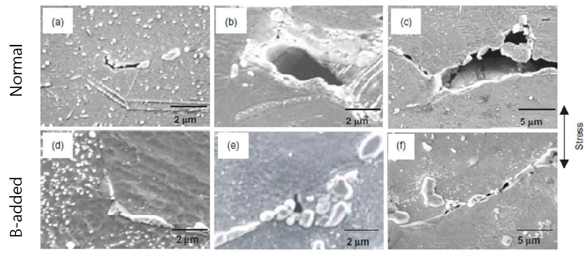
2. Actuation
: Break passive oxide layer

3. Transport of healing agent
: Diffusion of Cr solutes

4. Repairing (Driving force)
: Oxidation of Cr with Oxygen at the surface

4. Damage-tolerant self-healing metallic material

(f) B, BN segregation at 304 steel

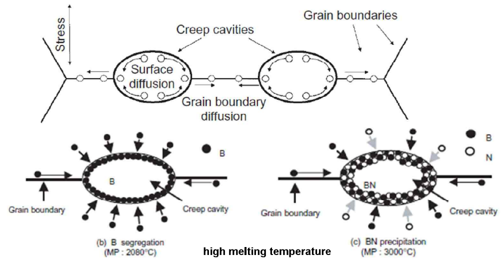


(a) t=238h(t/tr=0.71), (b) t=289h(t/tr=0.87), (c) tr=333h, (d) t=8,150h(t/tr=0.68), (e) t=10,200h(t/tr=0.86), (f) tr=11,900h.
t: creep time. tr: rupture time.

How to increase diffusivity?

4. Damage-tolerant self-healing metallic material

(f) B, BN segregation at 304 steel



➡ Surpressed the creep cavity surface diffusion of 304 steel

1. Damage
: Creep cavity

2. Actuation
: Heating

3. Transport of healing agent
: Diffusion into creep cavity

4. Repairing (Driving force)
: Segregation of B, BN

4. Damage-tolerant self-healing metallic material

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

1. Damage
: Fatigue crack

2. Actuation
: Dislocation moving across crack region

3. Transport of healing agent
: Pipe diffusion & Moving dislocation

→ Grain Boundary diffusion (100,000~1000,000) faster than Volume diffusion

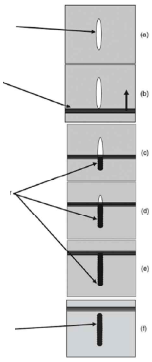
4. Repairing (Driving force)
: Dynamic precipitation

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)

5. Principle of self-healing material

"Metastability is the key" !

Possible mechanism

(1) Heat induced transformation

- Shape memory effect, Crystallization, Glass transition, Melting, order-disorder, Quasicrystal, …

(2) Strain induced transformation

- Superelasticity, Trip/Twin, metallic glass, …

(3) Magnetic-field induced transformation

- ferromagnetic shape memory materials, …

(4) Electric-field induced transformation

(5) Irradiation induced transformation

- Recombination of collision cascade, local melting, …

(6) Supersaturated solid solution

- Segregation, dynamic strain aging, …

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New approaches of
Self-healing Metallic Materials

1 & 2) defense for cracks 3) radiation self-healing

Homepage : http://espark.snu.ac.kr e-mail : espark@snu.ac.kr

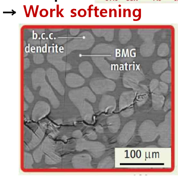
1) "Super-elastic Bulk Metallic Glass Composite"

Self-healing Metallic Materials with Recoverable 2nd phase

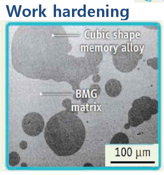
Homepage : http://espark.snu.ac.kr e-mail : espark@snu.ac.kr

Two different deformation behaviors of BMGC depending on 2nd phase

1) Ductile phase $Zr_{39.6}Ti_{33.9}Nb_{7.6}Cu_{0.5}Be_{12.5}$
→ Work softening

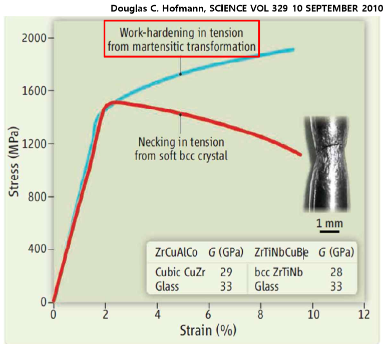


2) Transformation medi $Zr_{48}Cu_{47.5}Al_{4}Co_{0.5}$
→ Work hardening



< Tension >

Douglas C. Hofmann, SCIENCE VOL 329 10 SEPTEMBER 2010

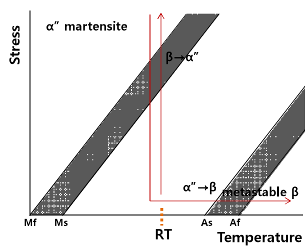


Development of New Ti-based BMGC with High Work-hardenability

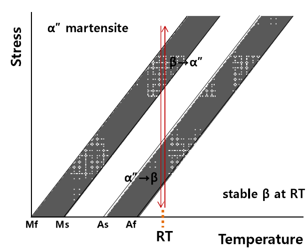
▷ Alloy system Cu-Zr-Al system ⇨ Ti-Cu-Ni system

	Cu-Zr-Al system	Ti-Cu-Ni system
Secondary phase	CuZr Metastable B2 phase at RT "Shape Memory Behavior"	Ti-X Stable B2 phase at RT "Superelastic Behavior"

Shape Memory Alloy (SMA)



Super-Elastic Alloy (SE alloy)



Phase transformation in Ti-based alloys : $B_2 \rightarrow M \rightarrow B_2$

- Alloy composition: Ti_{49}-Cu-Ni-X

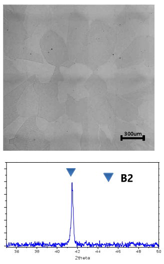
Φ3mm suction casting
-Fully crystalline B2

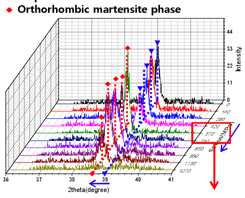
▷ Stress-induced phase transformation

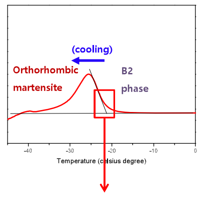
In-situ neutron diffraction measurement during compression

▷ Temperature-induced phase transformation

DSC measurement (during cooling)







Phase transformation stress = 570MPa

Martensite start T (Ms) = -22℃

➡ Novel Ti-based Super-elastic Crystalline Alloy

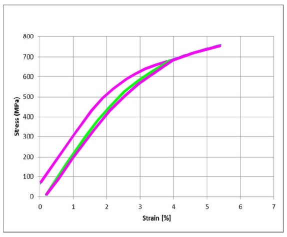
In-situ synchrotron diffraction analysis during tensile test

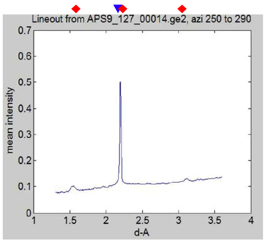
▷ Superelastic BMG composite: Reversible Phase Transformation Behavior

Ti-Cu-Ni-X Φ3mm
Water cooled Cu mold suction casting,

Loding → Unloading → Reloading

▼ Initial BCC phase in as-cast sample
◆ Deformed martensite phase





at APS beam line, ANL

2) "TWIP/TRIP High Entropy Alloy"

- Stress-induced phase transformable HEA -

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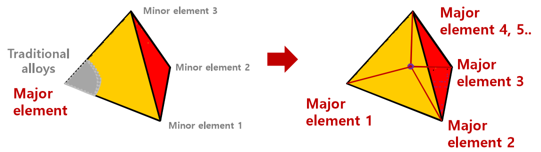
극저온 구조용 소재 개발의 글로벌 이슈

극한환경 조건으로의 휴먼존 확장을 위한 노력이 계속됨에 따라
"우수한 저온 인성을 갖는 극저온 구조용 소재 개발의 필요성"이 대두되고 있음

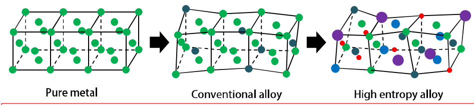
Basic concepts of high entropy alloy (HEA)



Conventional alloy system
Ex) 304 steel - $Fe_{74}Cr_{18}Ni_8$

High entropy alloy system
Ex) $Al_{20}Co_{20}Cr_{20}Fe_{20}Ni_{20}$

(1) Thermodynamic : high entropy effect
(2) Kinetics : sluggish diffusion effect
(3) Structure : severe lattice distortion effect
(4) Property : cocktail effect

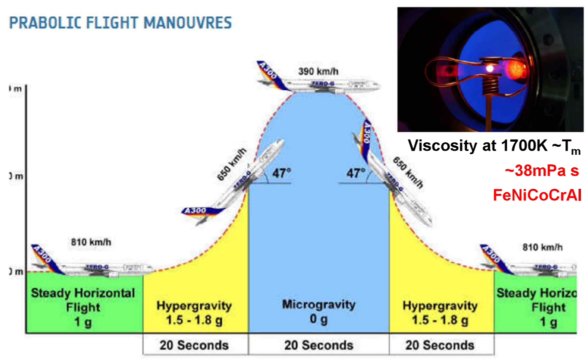


Severe lattice distortion → Sluggish diffusion & Thermal stability

Sluggish diffusion of high entropy alloy

DLR, Germany

Viscosity measurement of FeNiCoCrAl by EML in parabolic flight

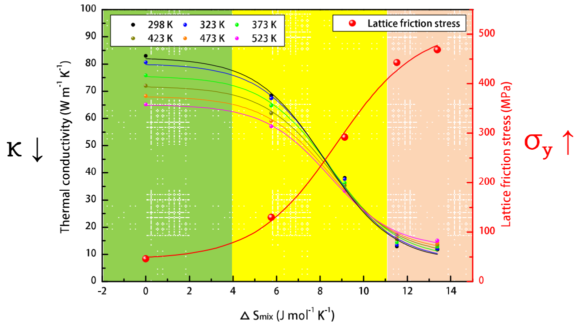


Viscosity at 1700K ~T_m
~38mPa s
FeNiCoCrAl

∴ High entropy alloy → relatively high viscosity in liquid state

Next Generation Polar Structural New Material: "High Entropy Alloy"

High σ_y/κ ratio



Development of ultra-tough alloy , especially at low temp.,

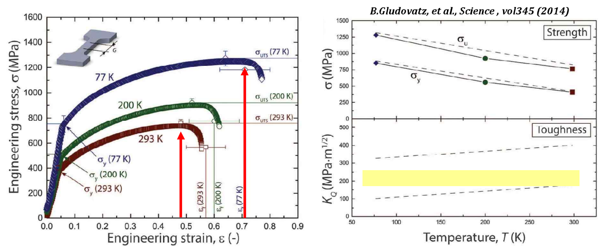
by design concept of high entropy alloy

Next Generation Polar Structural New Material: "High Entropy Alloy"

- Cryogenic properties of FCC high entropy alloys

1) Superior low temperature fracture toughness (~ 200 MPa·m$^{1/2}$)

2) Nano-twin operation keeps fracture toughness at room temp. even at low temp.

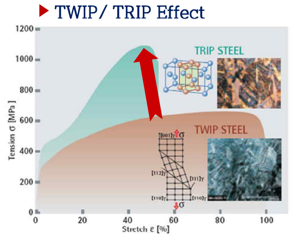


Development of ultra-tough alloy , especially at low temp.,

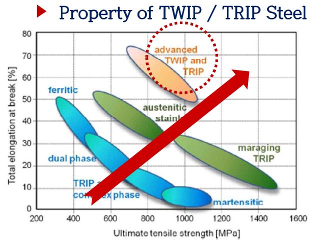
by design concept of high entropy alloy

Improve mechanical properties by introducing TWIP / TRIP effect

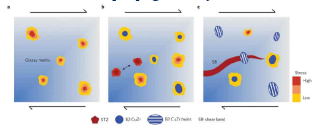
- TWIP/ TRIP Effect



- Property of TWIP / TRIP Steel



- Prevent crack propagation by TRIP

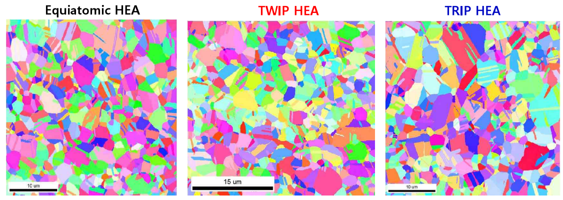


High toughness through TWIP or TRIP around cracks

"Development of TRIP high entropy alloy with high resistance to polar fatigue failure in the polar environment"

Development of TWIP/TRIP High Entropy Alloy

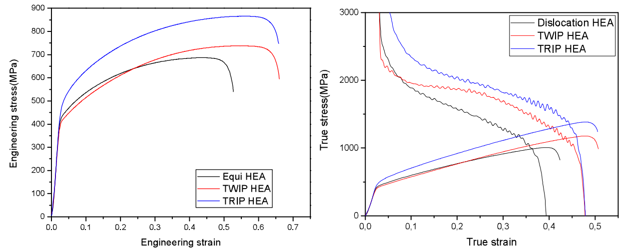
- Design of TWIP/TRIP high entropy alloy **without loosing yield strength**

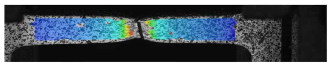


	Composition	Grain size (μm)
1	Equiatomic HEA	3.8
2	TWIP HEA	3.6
3	TRIP HEA	4.3

Development of TWIP/TRIP High Entropy Alloy

Ni-Co-Fe-Cr-Mn high entropy alloy

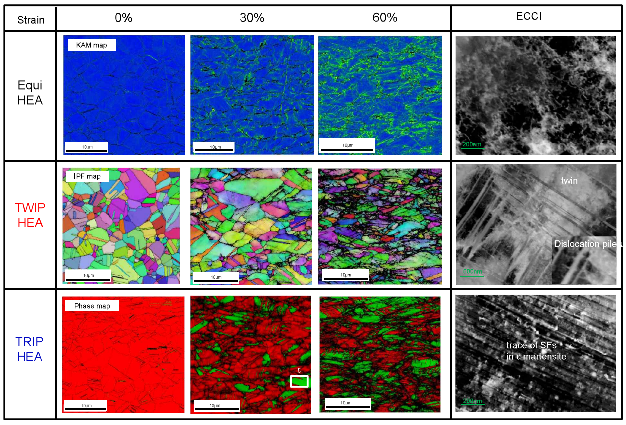




Considere criteria

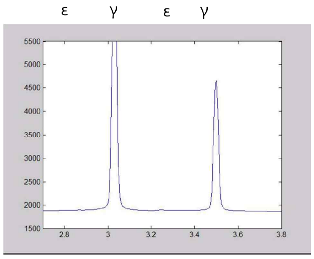
$\sigma = \frac{\partial \sigma}{\partial \varepsilon}$: Necking

Development of TWIP/TRIP High Entropy Alloy

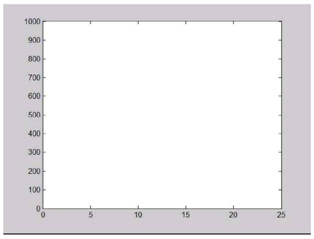


Development of TWIP/TRIP High Entropy Alloy

TRIP HEA



I(Q) vs. Q

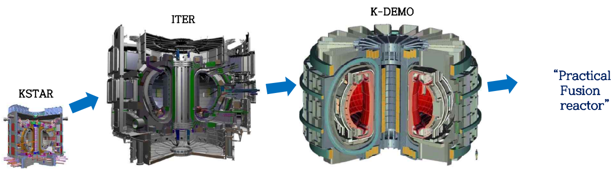


Stress (MPa) vs. Strain (%)

at APS beam line, ANL

Needs for developing novel material with high sustainability

Toward Next Fusion Devices



	ITER	DEMO	Reactor
Fusion Power	0.5 GW	2.5 – 5 GW	2.5 – 5 GW
Heat flux on 1st wall	0.1 – 0.3 MW/m²	0.5 MW/m²	0.5 MW/m²
Heat flux on divertor	~ 10 MW/m²	15 ~ 20 MW/m²	~ 20 MW/m²
Neutron load	0.78 MW/m²	< 2 MW/m²	~ 2 MW/m²
Displacement per atom	< 3 dpa	50~80 dpa	100~150 dpa
T retention limit	700 g (Administrative limit for fusion reactor)		
Dust limit	670 kg (Administrative limit for fusion reactor)		
Transmutation product rates at 1st wall	~ 10 appm He/dpa ~ 45 appm H/dpa		

3) "Radiation Self-healing High Entropy Alloy"

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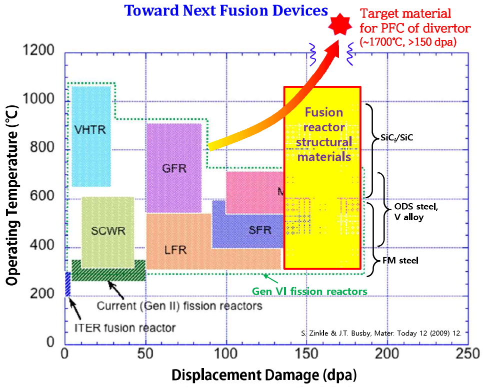
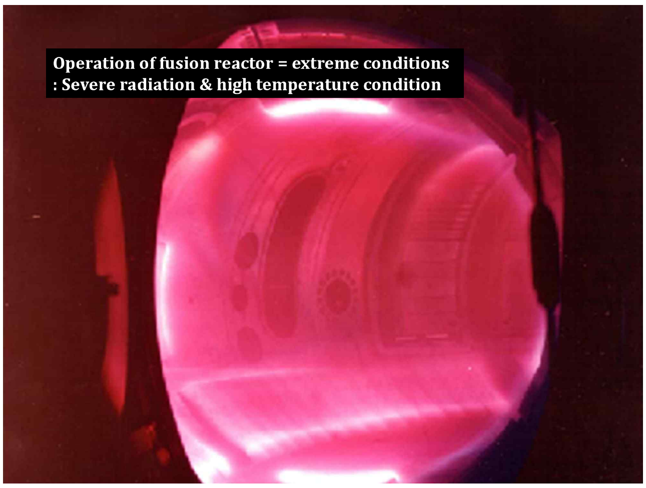
Needs for developing novel material with high sustainability

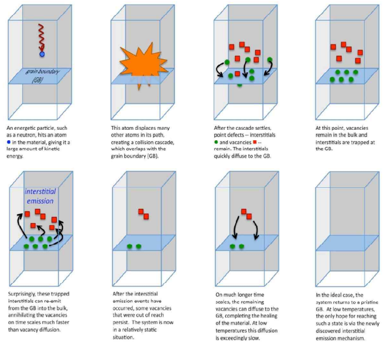
Toward Next Fusion Devices





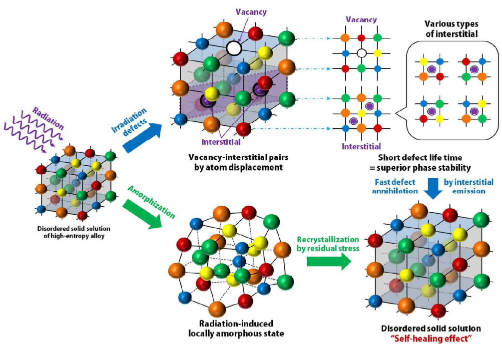
Development of radiation self-healing high entropy alloy

Nanocrystalline material **Irradiation damage**



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

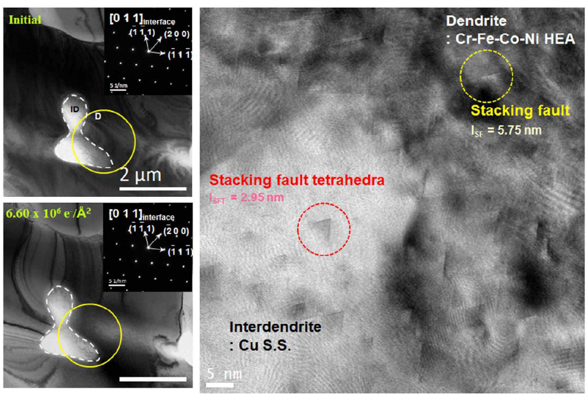
Development of radiation self-healing high entropy alloy



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

Development of radiation self-healing high entropy alloy

FCC Cu=Stacking fault tetrahedra vs FCC HEA = Stacking fault



"Innovation of new materials begins
when technological developments meet limits."