Bio-Inspired Engineering: Self-Healing Materials

Sayavur I. Bakhtiyarov
New Mexico Institute of Mining & Technology, USA
Outline

• Biological aspirations (anatomy of skin)
• Concept and definition
• Mechanism of crack propagation
• Crosslinking phenomenon
• First reports on self-healing materials
• Self-healing polymer composites
• High temperature self-healing metal composite
• Conclusions
Abbreviations

AES – Auger electron spectroscopy
BSE – back scattered electrons
EB PVD – electron beam physical vapor deposition
FRP - fiber reinforced polymer
HT – high temperature
LM – light microscopy
NCT – nanocarbon tubes
PAA - polyacrylamide
RE – reactive elements (La, Ce, Y, Hf, etc.)
SEM – scanning electron microscopy
SS – stainless steel
TBC – thermal barrier coating
TDCB - tapered double-cantilever beam
TGO – thermo-re-growth oxide
UV - ultraviolet
WDS – wave-length dispersive spectrometry
Anatomy of Skin

The skin is a dynamic organ containing a variety of tissues, cell types, and specialized structures, which together serve multiple functions important to health and survival. The skin interfaces with our dry, hostile environment and provides many functions crucial to survival, including protection against the elements (e.g., ultraviolet irradiation, mechanical and chemical injury, invasion by infection agents, and prevention of desiccation and dehydration) and thermoregulation.
Inflammatory reactions in the skin and wound healing

Healing proceeds temporally in three phases:
1) Substrate
2) Proliferative, and
3) Remodeling

The initial substrate phase encompassing the first 3 to 4 days after wounding, is so named because the cellular and other interactions lead to preparation for subsequent events. During this phase, vascular and inflammatory components prevail.

The proliferative phase (10 to 14 days after wounding) results in regeneration of epidermis, neoangiogenesis, and proliferation of fibroblasts with increased collagen (protein) synthesis and closure of the skin defect.

The final remodeling takes place over 6 to 12 months, during which time a more stable form of collagen is laid down to form a scar of progressively increasing tensile strength.
### Biomimetic self-healing inspiration in advanced composite structures (Trask et al, 2007)

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Mechanism of crack propagation at the interface (by Cook and Gordon)
Typical pattern of “main” crack propagation in:

a) Layered materials (composites, wood)

b) Homogeneous materials (metal, glass)
Bi-modal architecture of wood as a crack arrestor (Gibson & Ashby, 1997)

Utilization of the concepts arising in wood where sap channels act as crack arrestors to devise bimodal architectures which enhance the toughness of cellular solids.

Possible innovative materials developments for structural and multifunctional applications, allowing in addition the degree of freedom of multi-materials designs.
Definition of “Self-healing material” (from Wikipedia)

A self healing material is a **material** that has the built-in ability to partially repair damage occurring during its service life time.

Usually, a material's properties degrade over time due to damage (such as microcracks) on a microscopic scale. These cracks can grow and ultimately lead to **failure**. Self-healing materials address this slow failure through the inclusion of an "active" phase that responds the micro-damage by initiating a repair mechanism.
Crosslinking

**Crosslinked Polymer** - a polymer in which adjacent linear molecular chains are joined at various positions by covalent bonds.

Schematical crosslink reaction between crosslinker and polymer.
Crosslinking

Rheological studies on crosslinked PAA composite gel used in oilfield operations (Bakhtiyarov, 1976).
Electric fields inhibit stress cracks in metals

A strong electric field can stabilize the surface of metals and other electrically conducting and semiconducting crystalline solids, and inhibit the formation of fissures caused by mechanical stress (J. Materials Performance, April 2008).

The tip of the crack is a concentrator not only for the mechanical stresses and also for the electric current. The latter causes heating and even melting of the material around the crack tip.
Electric fields inhibit stress cracks in metals

(a) When mechanical stress is applied to the material under surface diffusion conditions, the so-called Asaro-Tiller or Grinfeld instability initiates the formation of cusp-like surface features that can evolve into cracked grooves. (b) The proper application of an electric field causes a change in surface morphology due to surface electromigration, which stabilizes or flattens the surface’s peaks and valleys. (c) Conditions are the same as in (b), but the electric current is turned off for a period of time, which initiates surface morphological instability, and then it is turned back on, which stabilizes the surface morphology. In all cases, the initial surface configuration is a low-amplitude sinusoidal shape perturbation from the planar morphology. Images courtesy of American Physical Society.
Self healing after radioactive damage (Popular Mechanics, May 2007, in Russian)

Computer simulations are demonstrated a possibility to develop self-repairing ceramic materials with the ability to recover after radioactive damage. This discovery can lead to development more effective components of nuclear power stations and more safe storages for nuclear wastes.

Zr stabilized with Y (Yttrium) inclusions remains undamaged after exposure to the strong radioactive effect. Its structural changes are distributed quite uniform, and material properties are not changed significantly.

In regular Zr the defects generate the damaging clusters (Ram Devanathan & William Weber).
The first report of a man-made self healing material was by the group of Dr. Scott White of the University of Illinois at Urbana-Champaign. They reported an epoxy system containing microcapsules. These microcapsules were filled with a (liquid) monomer. If a crack occurs in this system, the microcapsule will rupture and the monomer will fill the crack. Subsequently it will polymerise, initiated by catalyst particles (Grubbs catalyst) that are also dispersed through the system. This model system of a self healing particle proved to work well: the service life time of a structure made of such material will be significantly higher. Currently a number of research groups world wide is developing self healing mechanisms for essentially all materials classes (metals, polymers, ceramics, cemeticious, elastomeric and fibre-reinforced composite materials).
The autonomic healing concept (White et al, 2001, University of Illinois at Urbana-Champaign)

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.
Rupture and release of the microencapsulated healing agent

(a) Stress state in the vicinity of a planar crack as it approaches a spherical inclusion embedded in a linearly elastic matrix and subjected to a remote tensile loading perpendicular to the fracture plane. The left and right figures correspond to an inclusion three times stiffer ($E^* = E_{\text{sphere}}/E_{\text{matrix}} = 3$) and three times more compliant ($E^* = 1/3$) than the surrounding matrix, respectively. The Poisson's ratios of the sphere and matrix are equal (0.30).

(b) A time sequence of video images shows the rupture of a microcapsule and the release of the healing agent. A red dye was added for visualization. The elapsed time from the left to right image is $1/15$ s. Scale bar, 0.25 mm.

(c) A scanning electron microscope image shows the fracture plane of a self-healing material with a ruptured urea-formaldehyde microcapsule in a thermosetting matrix.
This scanning electron microscope image shows microcapsules used in self-healing polymers. The diameter of the microcapsules in the center of the image is approximately 100 microns.
Images of a self-healing test specimen with red dyed microencapsulated healing agent embedded in the epoxy matrix

(a) Virgin sample.
(b) Cracks form in the matrix wherever damage occurs. A crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action.
(c) The two halves of the specimen after it has been fractured into two pieces.
(d) On the crack faces, red healing agent is released from ruptured urea-formaldehyde microcapsules embedded in the epoxy.
Composites with hollow fibers
(Dr. Bond, University of Bristol, UK)

Hollow glass fibers (with ~200 μm spacing, filled with self-healing agents) embedded in carbon fiber reinforced composite laminate

Embedded hollow glass fibers (35 μm in diameter) can be filled with uncured epoxy polymer or chemical curing agent
A new self-healing concept with healing agent and catalyst encapsulated within double-walled nanotubes (NMT USA)
(a) Optical micrograph of microbubbles in CO$_2$/oil/water emulsion;

(b) SEM micrograph of hollow microcapsules made by UV-initiated polymerization;

(c) SEM micrograph of crushed microcapsules made by UV-initiated polymerization;

(d) SEM micrograph of solid microspheres made by thermally initiated polymerization.
SELF-HEALING via Electrohydrodynamic Coagulation

The technology has being tested initially with a system that contains two concentric cylinders (the inner one has a thin layer of insulating ceramic coating), with an electrical field applied to the system.

Between the two cylinders a colloidal dispersion of polystyrene or silica particles were used to repair defects that occur in the inner cylinder when high stress is applied.

When a defect occurs in the insulating coating, underneath metal was exposed to create high current density at the damaged site, causing colloidal particles to coagulate around the defect.

A schematic for a self-healing system that uses the electrohydrodynamic coagulation of particles to close a defect in a cylinder wall (Trau et al., 1997)
Recently, it was found that micellar copper oxide additions to viscoelastic lubricants significantly improve their anti-wear and friction reducing properties.

Under certain friction conditions the atomic copper forms a self-recoverable (“self-healing”) tribofilm on the cutting (drilling, machining) tool surfaces.

This film decreases the contact area between the workpiece and the tool, the friction coefficient, the temperature and tool wear. As a result, the tool life will be increased.
Bacteria as self-healing agent (Jonkers, 2007)

Bacteria as self-healing agent:

\[ 2 \text{Ca(CHO}_2\text{)}_2 + 2 \text{O}_2 \rightarrow 2 \text{CaCO}_3 + 2 \text{CO}_2 + 2 \text{H}_2\text{O} \]

Convert food to minerals (bio-cement)
Two-component self-healing agent ‘Green inside’:

1. Bacteria (catalyst)
2. Mineral precursor compound (chemical / 'food')

Bio-based self-healing concrete:

1. High crack-sealing capacity:
   - Less maintenance + repair
   - Prolonged service life constructions
2. Healing agent bio-based = ‘Sustainable’

Crack-healing: bacterial bio-cement production
Pitting corrosion is a localized form of corrosion by which cavities or "holes" are produced in the material. Pitting is initiated by:

a) Localized chemical or mechanical damage to the protective oxide film; water chemistry factors which can cause breakdown of a passive film are acidity, low dissolved oxygen concentrations (which tend to render a protective oxide film less stable) and high concentrations of chloride (as in seawater)
b) Localized damage to, or poor application of, a protective coating
c) The presence of non-uniformities in the metal structure of the component, e.g. nonmetallic inclusions.
Ceramic nanostructure coating is proposed to prevent pit growth on stainless steel (SS) at the sub-microscopic level.

To mitigate pit corrosion the steel can be coated with passive overlayer of $\text{Al}_2\text{O}_3$, $\text{SiO}_2$ or $\text{Ta}_2\text{O}_5$ (tantalum pent-oxide). However, single-layer films can fail because pinholes act as channels to quickly transport electrolytes through the film to the steel surface.

The substrate is coated with a multi-layered nanolaminate ceramic film that prevents pit growth at every new layer.
The metallurgical processes such as sintering and dynamic precipitation in response to loading conditions may initiate different levels of self-healing in Al alloys. Precipitation of crystalline materials into cracks occurs on a wide scale in geological processes, but biological processes governing the repair of bone and tissue are more relevant because of their inherent efficiency.

The service life of an Al alloy is related to its microstructure and the changes occur during service:

\[ \Delta \text{Service life} = f (\text{Service Environment}, \Delta \text{Microstructure}) \]

If the microstructure responds or adapts unfavorably to its conditions of loading and accumulates damage, then the service life will be reduced.
Development of High-Temperature Corrosion and Creep Resistant Nb, Mo and Cr Based Compositions with Protective Self-Healing Coating of Fe-45%Cr-4%Al-1%Ni-0.3%La Alloy

New Mexico Institute of Mining and Technology & Georgian Technical University
The traditional TBC do not exhibit any self-healing in contrast with the metallic bond coating.

These TBCs are made of a ceramic material and are the most critical part of the coating system for the lifetime of a coated component.

During heating and cooling, high stresses develop due to a mismatch between the coefficients of thermal expansion of the substrate and the different layers in the coating system.

The coating system life span is set by the development of crack patterns that coalesce and ultimately lead to failure.
TBC requirements

The selection of TBC ceramic materials is restricted by some basic requirements (Cao et al, 2004):

1) High melting point
2) No phase transformation between room temperature and operation temperature
3) Low thermal conductivity
4) Chemical inertness
5) Thermal expansion matching with the metallic substrate
6) Good adherence to the metallic substrate
7) Low sintering rate of the porous microstructure
Heterogeneous architectured metal / metal / ceramic high temperature coating systems

- **Self-organizing TBC**
  - Coating
  - Substrate

- Scar ($\text{Cr}_2\text{O}_3$, Fe, Al, Y, La complex oxide)
- TGO ($\text{Al}_2\text{O}_3$) sub-layer
- HT corrosion resistant alloy (Fe-Cr-Al-RE) (RE = La, Y)
- HT creep resistant metal (Nb, Mo, Ta, Cr)
Self-organizing, protective oxide scales on the Fe-44%Cr-1%Ni-4%Al-0.3%La alloy surface (Kutelia & Bakhtiyarov, 2008)

Amorphous Beilby layer formation due to the self-organizing dissipative processes on the surface of an Fe-Cr-Ni-Al-La alloy with high (>40%) chromium content

The Al$_2$O$_3$ layer is characterized by high adherence with metallic substrate and provides protective features against both high temperature (1200$^\circ$C) oxidation of the matrix and resistance to abrasion.

A thin (several microns) scale is formed by the pretreatment alloy’s surface at 1200$^\circ$C.
Electron-diffraction patterns (the electronograms) obtained by reflection from the polished surface from different depths

A schematic of structure changes by thickness on mechanical polished Fe-44%Cr- 4%Al-0.3%La alloy surface.

a) 50Å (the structure is amorphous);

b) 300Å (in Roentgen-amorphous condition);

c) 1300Å (polycrystalline, desegregated structure)
The surface layer (≤1μm thickness) of the mechanically polished specimen of Fe-44%Cr-1%Ni-4%Al-0.3%La alloy consists of the amorphous Beilby layer. Its adjacent matrix layer, crushed due to the plastic deformation, formed an entropy “excited” functional system, which at 1200°C forms an oxide surface layer with a micro-wrinkles modulated structure of uniform thickness in the form of mixture of nano-crystallites (100-500nm) made of oxides of atoms constituting the basic metallic matrix.

SEM images of the Fe-44%Cr-1%Ni-4%Al-0.3%La specimen surface oxidized in the air at 1200°C for 5 hours. The samples have previously been mechanically polished up to the formation of Bailby layer.
Beneath this layer a thin alumina scale was formed. An increasing of the oxidation temperature (~1400°C) causes the regrowth of nanocrystallites and also the recrystallization processes accompanied by solid-phase reactions between oxide nano-particles. This leads to the scale delamination at the superficial oxide thin uniform alumina layer interface.

SEM images of the Fe-44%Cr-1%Ni-4%Al-0.3%La alloy after oxidation cycles 1200°C/5 hours + 1400°C/1 hour, where the relatively loose superficial structure is removed.
The results of tribological tests: a) & b) dependence of friction coefficient and wear intensity on friction velocity respectively; curves plotted for the specimens of investigated alloy before and after oxidation at elevated temperature.

Pre-oxidization treatments where a thin oxide ceramic layer was formed on the disk surface can be useful in reducing friction, wear and galling.
High-Temperature Self-Healing Coating

SEM micrographs showing the structure of an EB-PVD Fe-45%Cr-1%Ni-4%Al-0.3%La overlay coating deposited on the substrates:

a) single crystal of Nb

b) single crystal of Mo
SEM images and WDS spectra of the EB-PVD Fe-45%Cr-1%Ni-4%Al-0.3%La areas deposited at 650°C of single crystal substrate of Nb (110): a) the solidified drop of evaporated alloy splashed on the coating surface; b) higher magnification of the area indicated on (a) which demonstrates the superfine graininess of coating structure; c) WDS spectrum of the solidified drop; d) WDS spectrum of the marked area on the coating.

High-Temperature Self-Healing Coating
SEM images and WDS spectra of the EB-PVD Fe-45%Cr-1%Ni-4%Al-0.3%La areas deposited at 650°C of single crystal substrate of Mo (110): a) the solidified drop of evaporated alloy splashed on the coating surface; b) higher magnification of the area indicated on (a) which demonstrates the superfine graininess of coating structure; c) WDS spectrum of the solidified drop; d) WDS spectrum of the marked area on the coating.
Optical micrograph showing the superfine graininess EB-PVD Fe-Cr-Ni-Al-La overlay coatings deposited at 650°C on the surface of single crystals:

 Nb (110)  
 (a and b)

 Mo (110)  
 (c)

High-Temperature Self-Healing Coating
Scanning electron BSE image of the area with the crack in the thin ($\lesssim 10 \mu m$) coating of EB-PVD Fe-Cr-Ni-Al-La coated on the single crystal of Nb (110); b) image of the same area after specimen exposure at $1200^\circ C$ during one hour in air; c) higher magnification micrograph of the area indicated on (b) shows more details of the microstructure of healed microcrack; d) optical micrograph of the same area (c) shows the scars of healed crack.

High-Temperature Self-Healing Coating
SEM micrograph and WDS spectra of EB-PVD coating on the surface of Nb (110) monocrystal showing the microstructure and chemical composition of self-healed crack during the exposure of the specimen at 1200°C for one hour in air.

a) BSE micrograph of the crack underwent thermal activated self-healing.

b) WDS spectra of the area A in a distance from the crack.

C) WDS spectrum of area B of the healed crack.
Optical micrographs showing:

(a) Surface

(b) cross section of EB-PVD Fe-Cr-Al-Y overlay coating deposited on the low alloyed chromium.
SEM–BSE micrographs of the cross-section of EB-PVD Fe-Cr-Al-Y overlay coating deposited at 700°C on a polycrystalline low alloyed Cr specimen before (a and c) and after (b and d) specimen exposure at 1200°C for one hour in air, showing the full healing of the coating growth defects in the form of inter-columnar channels.

High-Temperature Self-Healing Coating
Optical micrographs showing:

a) the cross-section of an EB-PVD Fe-Cr-Al-Y overlay coating deposited on a polycrystalline low alloyed chromium specimen before high temperature exposure;

b) the same area after specimen exposure at 1200°C for one hour in air and cooling down to room temperature.
Optical micrographs showing:

a) the area of top surface coating, the specimen before high temperature exposure

b) the same area of the surface after specimen exposure at 1200°C during one hour and cooling down to room temperature
a) SEM-BSE micrograph showing the composition of microstructure that developed on cross-section surface of the low alloyed specimen coated with EB-PVD Fe-Cr-Al-Y alloy. The image after oxidation at 1200°C during one hour in air.

b, c, d) WDS spectra of the areas A, B, C.
a) SEM image of the specimen morphology with polished surface after oxidation at 1200°C with the cycles of 1+4+5 hours; b) the magnified image of the area B (the area with spalled outer scale). c) Auger spectrum of the area A; d) Auger spectrum for the area B.

High-Temperature Self-Healing Coating
a) SEM-BSE image

b) Optical micrograph of the surface EB-PVD Fe-Cr-Al-Y coating on the polycrystalline substrate of low alloyed chromium after oxidation cycles at 1200°C during one hour and cooling down to room temperature + exposure at 1400°C for 30 min in air and again cooling down to room temperature.
a) SEM-BSE magnified image of the area presented on previous Figure

b, c) WDS spectra of the area marked on a, A and B respectively

High-Temperature Self-Healing Coating
CONCLUSIONS

This work presents the possibility to realize the self healing mechanisms for heterogeneous architectured metal/ceramic high temperature sandwich thermal barrier coating systems on the surfaces refractory metals by analogy of wound healing in the skin.

Self-healing materials must address a slow failure through the inclusion of an "active" phase that responds the micro-damage by initiating a repair mechanism

The best “self-healing” approach – “bio-inspired” approach
Research staff and students at New Mexico Tech and Georgian Technical University for participation in experimental work

The financial support received from NASA EPSCoR for high temperature self healing coating materials development project
Thank you!

Questions?