

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Self-Healing in Titanium Alloys: A Materials Science Perspective

Paul Sunday Nnamchi and Camillus Sunday Obayi

Abstract

Self-healing materials (SHM's) is an emerging class of smart materials, which are capable of autonomous or spontaneous repair of their damage under external stimuli, such as heat, light, and solvent, to the original or near original functionalities much like the biological organisms. The emergence of self-healing in metallic materials presents an exciting paradigm for an ideal combination of metallic and biological properties. The driving force behind this effort is to decrease the consequences of accidents, reduction of cost and extending the service life of metallic components. While previous reviews have focused on self-healing in polymers, composite, concrete and cementous materials, and ceramic, discussions about self-healing in metallic materials remains scarce and the survey of literatures suggests Ti-based self-healing materials known to be biocompatible in human body is rare. The present chapter examines the art of self-healing in titanium-based alloys with the scope to provide an overview of recent advancements and to highlight current problems and perspectives with respect to potential application.

Keywords: self-healing metals, self-healing coating, Ti-based alloys, shape memory effect (SME), autonomous repair, damage, design strategy

1. Introduction and background

Historically, solving material reliability issues has been an old and long term quest of material scientist and engineers, due to their implications for material safety. Considering the fact that structural materials degrade irreversibly over time owing to proliferation of damage like microscopic cracks: the growth of which eventually results in failure. And most times, these internal defects or damage are deep inside materials and difficult to perceive and repair. Recently, there has been a huge interest in materials that can self-heal, as this property can potentially extend materials lifetime, minimize replacement costs, and improve product safety and reliability [1]. Thus, having materials with intrinsic self-repair capabilities—a sort of biomimetic healing functionality, may then allow failures to be averted and the useful lives of components and structures to be extended [2, 3].

Although self-healing is an exclusive specialty of living organisms of biological origin and not easy to put in place in non-biological materials, continuous efforts are now being made to mimic natural materials and to integrate self-healing capability into polymers and polymer composites. Self-engineered healing properties, which are applied in closing and healing crack initiated in a material during its utilization, have been described in cementous [4] and polymer materials [5]. Self-healing approaches mostly gained by surface modification [6–9] or by the creation

of a composite material with some other smart material like NiTi [10, 11] are been utilized in metals and other inanimate materials. For example, damage to oxide films, which normally protect the surfaces of metals such as aluminum (Al) and titanium (Ti) from corrosion, can be repaired by reoxidation in air, which can be seen as a form of self-repair. Also identified are the self-healing properties obtained by encapsulating a solder material into a metallic matrix [11–13]. Self-healing behavior was also observed in a commercial Al alloy after suitable heat treatment [14] and some other precipitation-forming systems [15, 16]. Healing can be initiated by means of an external source of energy as was shown in the case of a bullet penetration [17] where the ballistic impact caused local heating of the material by allowing self-healing of ionomers.

There are several different strategies to impart self-healing functionality that have been developed and the number of publications dealing with various aspects of self-healing materials has increased markedly in recent years. On the whole, the vast majority of the articles deal with polymer composites and cementous materials. Research in the field of metallic systems is still in its infancy. However, the emergence of self-healing in metallic materials, such as titanium adjoined to be biocompatible and explored here presents an exciting paradigm for an ideal combination of metallic and biological properties in application traditionally dominated by metallic materials. Depending on the method of healing, self-healing in metallic system can be classified into two categories: (i) intrinsic ones that are able to heal cracks or repair damage by the metals themselves and (ii) extrinsic in which healing agent has to be pre-embedded.

This chapter begins with an overview on the importance of titanium as an engineering of self-healing materials. Since all processes of self-repair, including healing in living bodies depends on rapid transportation of repair substance to the injured part and reconstruction of the tissues, Therefore, the knowledge of basic principle of solid state diffusion is essential for understanding the self-repair processes, such as phase transformation, precipitation and shape memory effects taking place titanium and other alloys, were briefly discussed. The chapter concludes by considering future research.

2. Titanium: A special engineering material

Titanium has been an important development in the history of non-ferrous industry. Titanium is an attractive material with excellent corrosion resistance and high strength-to-weight ratio. It combines the strength of iron and steel with the light weight of aluminum, which accounts for its widespread use. Industrial applications of titanium materials have recently expanded widely in many areas such as the aerospace, chemical plants, automobiles, and aviation industries, and even in high performance sports equipment, and in the medical field for bone. Their biological compatibility is particularly of interest to the medical industry implants and replacement devices [17]. Currently, the chemical industry is the largest user of titanium due to its excellent corrosion resistance, particularly in the presence of oxidizing acids. The ballistic properties of titanium are also excellent on a density-normalized basis. Some physical properties as compared with other engineering materials by Hanson are presented in **Table 1** [18]. Detailed discussions on other applications of titanium in other areas can be found elsewhere [18, 19].

Besides the areas mentioned above, building applications such as exterior walls and roofing material have emerged as a new market for titanium. Using CP titanium as building material has become especially popular in Japan [20]. One example is the Fukuoka Dome, built in 1993, which is covered with titanium roofing,

retractable for multi-role and all-weather purposes (**Figure 1**) [20]. Each of these building projects uses large quantities of CP titanium leading to the increased usage in the civil engineering area in Japan. Another “new area” in which titanium use is growing is the area of consumer products, such as spectacle frames, cameras, watches, jewelry, and various kinds of sporting goods. The largest application in the area of sporting goods is golf club heads. Other examples are tennis rackets, bicycle

Physical Property	Titanium	Aluminium	Copper	Iron	Magnesium
Melting point (°C)	1665	660	1083	1535	650
Density (Mg/m ³)	4.51	2.70	8.94	7.86	1.74
Thermal conductivity (W/mK)	16	239	384	71	147
Electrical resistivity (nΩm)	482	26.8	17.2	97.1	44
Specific heat (J/KgK)	528	883	389	456	1026
Magnetic susceptibility (X10 ⁻⁶)	+ 3.4	+ 0.65	-0.086	Ferro magnetic	+ 0.55
Elastic modulus (GPa)	110	70	120	200	45

Table 1.
Physical properties of titanium compared with other metals [18].



Figure 1.
(a) Aerial approach view of the Fukuoka dome, built in 1993, which is covered with (b) titanium roofing, retractable for multi-role and all-weather purposes.

Alloy	Nominal Composition	Density	Coefficient of Expansion	Thermal Conductivity	Resistivity	Temperature Coefficient of Resistivity	Specific Heat	Magnetic Susceptibility	Elastic Modulus
		(Mg/m ³)	(x10 ⁻⁶ /K)	(W/[mK])	(nΩm)	(20-100°C)	(J/[KgK])	(x10 ⁻⁶)	(GPa)
IMI 115-160	Commercially pure	4.51	7.6	16	482	0.0036	528	+3.4	110
IMI 260/262	Ti-0.15Pd	4.52	7.6	16	482	0.0036	528		
IMI 230	Ti-2.5Cu	4.56	9.0	13	700	0.0026			110
IMI 318	Ti-6. Al-4V	4.42	8.0	5.8	1680	0.0004	610	+3.3	110-125
IMI 550	Ti-4Al-4Mo-2Sn-0.25Si	4.60	8.6	7.9	1590	0.0004			117
IMI 551	Ti-4Al-4Mo-4Sn-0.25Si	4.62	8.4	5.7	1700	0.0003	400	+3.1	112
IMI 685	Ti-6Al-5Zr-0.5Mo-0.25Si	4.45	9.8	4.8	1670	0.0004			124

Table 2.
Physical properties of titanium and some of its alloys [18].

frames, spikes in sprinters. Their low coefficient of thermal expansion is also an important factor. The ballistic properties of titanium are also excellent on a density-normalized basis. Future applications are likely to be in the areas of steam turbine blading, flue gas desulphurization plant consumer products and many marine applications. Some of the basic characteristics of titanium and its alloys are listed in **Table 2** in [18] and compared to those of other structural metallic materials based on Fe, Ni, and Al. Detailed discussions on other applications of titanium in other areas can be found elsewhere [4].

3. Crystallographic structures in titanium metal and alloys

Generally, all property of materials depends directly or indirectly on the type of crystallographic phase and its constructions. The stable structure of pure Ti is the hexagonal close-packed (hcp) structure (α phase) at room temperature, which transforms to the body-centered cubic (bcc) structure (β phase) at high temperature. Apart from these stable phases, other metastable phases can emerge in a quenched alloy such as (α') martensite with hexagonal structure, martensite with orthorhombic (α'') structure or the β phase [20] or an omega (ω) phase. There are two types of omega ω phases with hcp structure, one is athermal, which forms during quenching from β -phase at high temperature and this type is cooling rate dependent. The other is isothermal ω phases, which precipitate during aging at certain temperatures. However, the exact relationship between the two omega ω phases and the α'' martensite phase for reversible transformation is still a subject of many research studies.

For this, interests in titanium-base alloys as structural materials has inspired several studies of their phase relationships. These have provided the background essential to the development of commercial alloys, but have also revealed some unexpected, and still to some extent unexplained, aspects that are of considerable scientific interest [2]. Although the exact transus point is dependent on the composition and processing treatment for the alloy, for alloyed Ti based materials, the transformation of crystallographic phase could also be driven by alloying elements.

Titanium alloys are stabilized by solute elements that have strong effect on the transformation temperature. Alloying elements of titanium are typically grouped based on their effect on the beta-transus temperature. They are often termed as neutral, alpha stabilizers, or beta-stabilizers. According to this classification scheme the alpha stabilizing alloying elements extend the room temperature hexagonal alpha phase field to elevated temperatures, while beta-stabilizing elements shift the high temperature beta phase field to lower temperatures. Neutral elements have only minor influence on the beta-transus temperature. Among the alpha stabilizing elements aluminum is by far the most important alloying element of titanium. The interstitial elements oxygen O_2 , nitrogen N, and carbon C also belong to this category, which are referred to as α -stabilizers [20] (see **Figure 2**).

Some of the high temperature β phase stabilizing elements are Nb Mo; V; W; Fe; Cr; Mn; Co; Cu; Si, H and Ta at room temperature. For β -stabilizers, a minimum concentration β element is required to fully stabilize the β -phase following a quench from the high temperature. The β stabilizing elements are categorized into two groups, namely:

- i. β eutectoid stabilizers are elements (which lead to a partially stabilized β phase) such as Fe; Cr; Mn; Co; Cu; Si and H.
- ii. β isomorphous forming elements are heavy refractory BCC elements such as Mo; V; W; Nb and Ta.

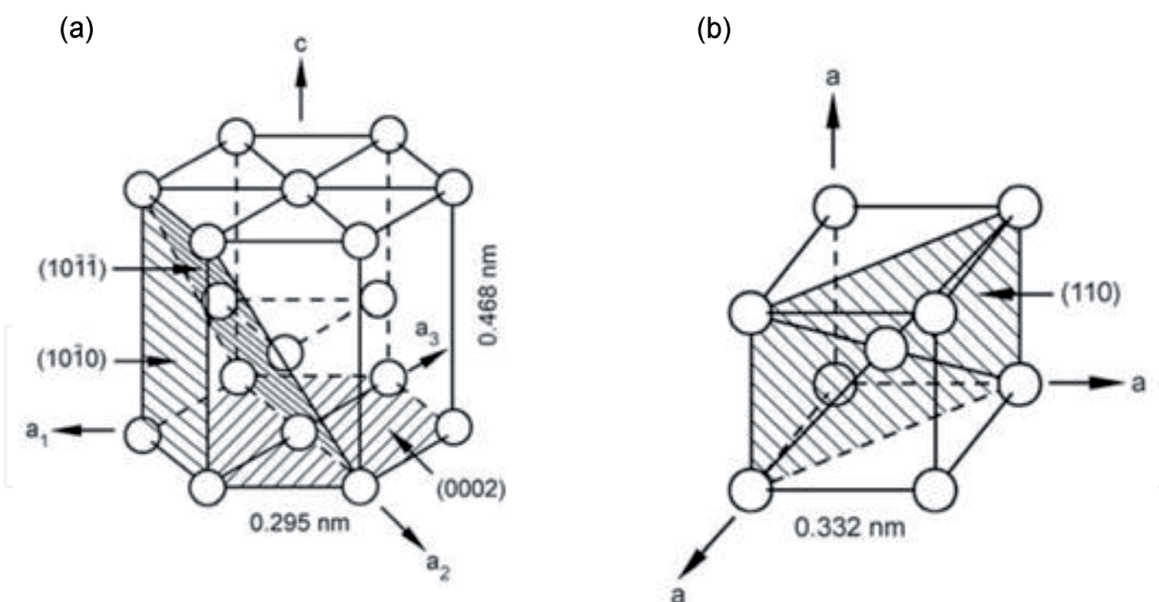


Figure 2.
 (a) Unit cell of α type titanium phase (b) unit cell of β type titanium phase [21].

The β phase can be easily transformed to hexagonal (α' and ω) or orthorhombic (α'') phases depending on the contents of the β stabilizing elements at room temperature. The (α'') phase has more slip systems than that in the hexagonal phases but fewer than in the β phase.

Although it might be that no metallic element is purely neutral, some elements are classified as neutral because they have a minor influence on the transus temperature. They can lower the β transus slightly, but again increase it at a higher concentration. These elements include Sn, Zr and Hf, which may slightly lower the α/β transformation temperatures after certain threshold concentrations. Zr and Sn are the commonly used neutral stabilizing elements. Zr and Hf are isomorphous with titanium and therefore exhibit the same allotropic phase transformation from β to α and are completely soluble in both the α and β phases. Zr also substitutes titanium in a multicomponent alloy and thereby indirectly has a α stabilizing effect [20].

4. Some self-healing assisting phenomena in titanium metal and alloys

4.1 Phase transformation in titanium metal and alloys

Phase transformation occurs whenever a materials system is not at equilibrium, or changes its microstate, as a result of external constraints such as pressure or temperature. In effect, these materials adopt different crystal structures favorable for the minimization of their free energy. In general, the microstructural features and the order in the system changes, leading to variations in most of the important properties. By so doing, phase transformation provides an effective way to modify the microstructure of solids. If it can be activated by a mechanical or other physical force, it becomes part of the deformation process and directly affects the properties of materials as well [22].

In CP titanium and titanium alloys, the most common equilibrium phases are those of α and β , phases. The transformation of high temperature phase can occur by martensitic or by a diffusion controlled nucleation and growth process depending on cooling rate and alloy composition. Their relationship was confirmed for Zirconium by Burger [23, 24] and later for titanium by [22]. This Burgers

relationship is closely obeyed for both the martensite transformation and the diffusional transformations (see **Figure 3**).

Thus, during phase transition from β to α , several slip systems operate within the α titanium alloys system. The most common slip direction is $\langle 11\bar{2}0 \rangle$. The \vec{a} direction slip occurs in one (0002) basal plane, three $\{10\bar{2}0\}$ prism planes, and six $\{10\bar{1}1\}$ pyramidal planes [21, 26–29]. They are therefore responsible for the four independent slip systems. The fifth slip system required for homogeneous deformation of polycrystals (Von-Mises criteria) is provided by the two basal slips that occur in the $\langle 112\bar{3} \rangle$ direction and in the $\{11\bar{2}2\}$ plane. If the slip systems are unable to operate, twinning occurs in α titanium. The main twinning modes are $\{10\bar{1}2\}$ and $\{11\bar{2}1\}$ in tension and $\{1122\}$ in tension and $\{1122\}$ in compression loading [21, 30–32].

4.2 Martensitic transformation in titanium metal and alloys

Phase transformation provides an effective way to modify microstructure and property of solids. It becomes part of a deformation process, when it can be activated by mechanical or other physical forces. Titanium and its alloy undergo a series of stable and metastable allotropic transformations, depending on alloy elements and process. The exact transus point is dependent on the composition and processing treatment for the alloy. Apart from the stable phase(s), other metastable phases can emerge in a quenched alloy such as martensite with hexagonal structure, martensite with orthorhombic structure or the metastable β phase (see **Figure 4**).

Some striking characteristics distinguish martensite transformations from any other [34]. First, the martensite phase is either a substitutional or interstitial solid solution. Secondly, the transformation takes place in a very short time (i.e.) very rapid. This can only be measured by high speed cameras. The complexity inherent in its measurements is an added problem to its study. The third is that it is accompanied by a shape change (surface relief) of a definite value. This has been confirmed metallographic ally by scratch line test [34]. The fourth is that martensite crystal has a specific habit plane; interfacing between the parent phase and martensite phase

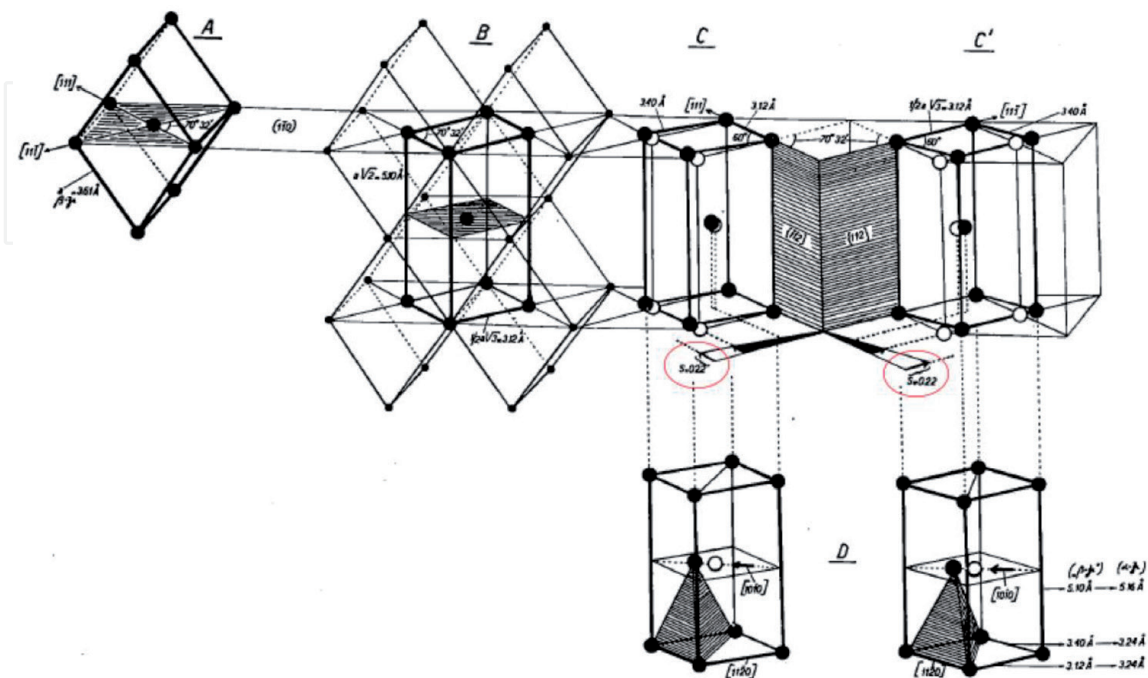


Figure 3. Schematic illustration of the Burgers' lattice correspondence model of bcc-hcp transformation. The two simultaneous shears are marked by the red ellipses [25].

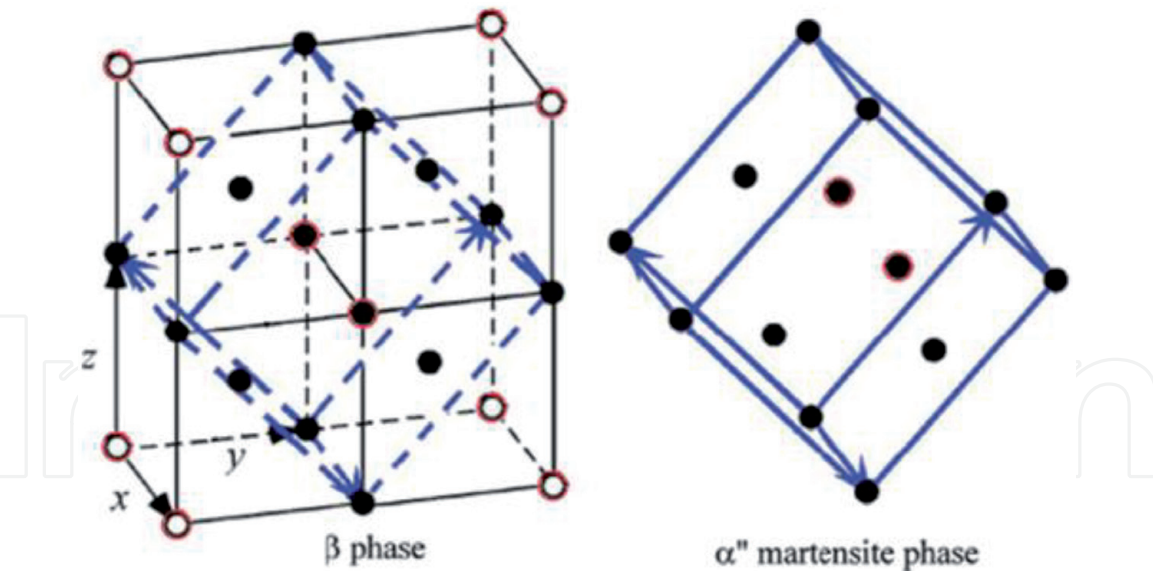


Figure 4.
A schematic illustration showing the lattice correspondence between the β and α'' phases, after Kym et al. [33].

which lie along the shear plane during the transformation. This implies that an orientation relationship exist between the two phase lattices. The presence of lattice defects will necessarily exist in martensite crystal due to shearing. The list of alloy components where martensitic transformation can be exploited are not exhaustible and still growing with research in the field of Titanium [35–37].

The recent innovative drive for Ti-alloys has drifted to many other areas such as the formation of SIM for electrical appliances, GUM metal for industrial applications, bio-implants resulting from its excellent compatibility with body tissues, better the mechanical and physical properties. There is an agreement among researchers that the formation is due to deformation by twinning (A twinning process is shown in **Figure 5** as culled adapted from [38]) of β -phase material to a type of martensite α'' with

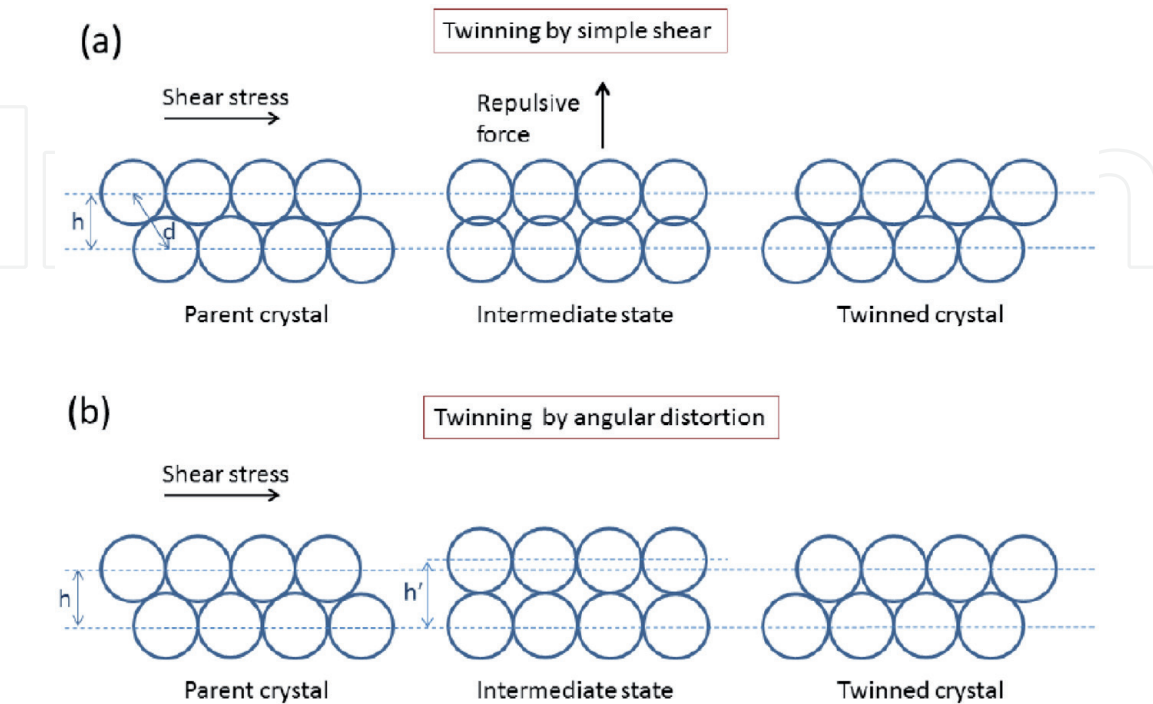


Figure 5.
Schematic 2D representation of a collective displacement of the atoms during deformation twinning according to (a) simple shear, (b) angular distortion.

orthorhombic structure. It is also thought that over a narrow compositional average the β -phase material is said to transform to martensite under an applied stress.

4.3 Shape memory effect and super-elasticity in titanium alloys

Shape Memory Alloys (SMAs) are special materials with great potential in various engineering applications since they possess a number of unique characteristics, including superior energy dissipation capacity compared to normal metallic materials [39]. Other beneficial properties, apart from SMEs, including superelasticity, favorable damping ability and other important characteristics of shape memory alloys, allow it to be applied in a wide range of fields, including electronic, chemical, medical devices, electricity, aerospace, etc. [40].

The value and demand of SMAs was not positively understood for most engineering and technological applications until William Buehler and Frederick Wang discovered the shape memory effect (SME) in a nickel-titanium (NiTi) alloy in 1962 [41]. Thereafter, the use of SMAs, has expanded and the research interests and patents have become quite large. Examples of the possible beneficiaries of these materials abound in a variety of fields, such as automobile and mechanical engineering applications [42, 43], automotive [42], aerospace [44], mini actuators and micro-electromechanical systems (MEMS) [45], robotics [35], biomedical [36] and even in clothing/fashion industries [37]. Titanium (Ti) alloys are one of the most important SMAs and until now, development of new Ti-based SMAs is still one of the most important directions of metal intelligent materials. The Ti-Nb based [35–37, 45], Ti-Ta based [46], Ti-Mo based [46–48] and Ti-Zr based [49] SMAs are developed in recent years.

The interest in using shape memory alloys (SMAs) stems from the fact that they can “remember” their original shape. When subjected to an external force above a threshold, they exhibit stress-induced martensitic transformation from austenite into martensite through twinning, and can recover the apparent permanent strains, returning to the original form. An illustration of the superelastic response in shape memory alloys (deformation at a temperature N austenite finish temperature A_f). This important attribute exhibited by many titanium based alloy can be exploited to accelerate the self-healing process in metallic materials. In addition by adjusting the hysteresis width can allow materials scientists to precisely adjust temperature change ΔT during the self-healing process. One of the probable set back is the functional degradation in properties that manifested as a reduction in the superelastic strains (ϵ_{SE}) and accumulation of residual strains ($\epsilon_{residual}$).

4.4 Diffusion in titanium metals and alloys

It is well known that atoms in almost all metals and alloys crystallize or has a tendency to pack in dense structural arrangement at room temperature, due to the strong bond that bind atom together in a metallic substance. This architecture determines how fast or how slow a healing mechanism would autonomously respond when a metallic component fails. Therefore, it is rational to deduce that triggering autonomous self-healing should be easier if the rate of diffusion of the part is high enough to be transported to the point where it fails. The molecular diffusion or atomic transport of matter by diffusion is represented ideally by the net flux, J , of atoms per second per unit area of reference plane in opposite directions ($\pm x$) in the presence of a concentration gradient, dc/dx , as given by Fick's first law:

$$J = -D(dc/dx). \quad (1)$$

where D is the diffusion coefficient, given by:

$$D = D_0 \exp.(-Q/RT). \tag{2}$$

D_0 (the frequency factor in cm^2/s), Q (the activation energy for diffusion in kJ/mol) and R (the gas constant, 8.314510 J/Kmol) are all constants, so the only variable is the temperature T , in Kelvin. In other words, $\ln D$ vs. $1/T$ forms a single straight line. In the case of Ti, higher temperature induces thermal diffusion needed to increase the kinetic energy needed to overcome the binding energy of the metallic substance. In addition to Vacant lattice sites or other in homogeneities within a metal, molecular transport can also be influenced by pressure and electrical and magnetic activations, chemical process and mechanical agitation of atoms.

There have been several improvement in the study of diffusivity in the case of in titanium alloys, beginning with the work documented in German by Zwicker in 1974 [50]. On transformation from the α (hcp) to the β (bcc) phase, the diffusivity shows some changes. With respect to the widely used Ti-6Al-4V alloy. Liu and Welsch in 1987 studied the diffusivities of oxygen, aluminum, and vanadium in α and β titanium [33]. Zwicker observed in the plot that the self-diffusion of titanium in the β phase is about three orders of magnitude faster than the self-diffusion in the α phase [50] (see **Figure 6**). The diffusion rates of substitutional elements in the β phase can be either slower or faster than the self-diffusion of titanium [33].

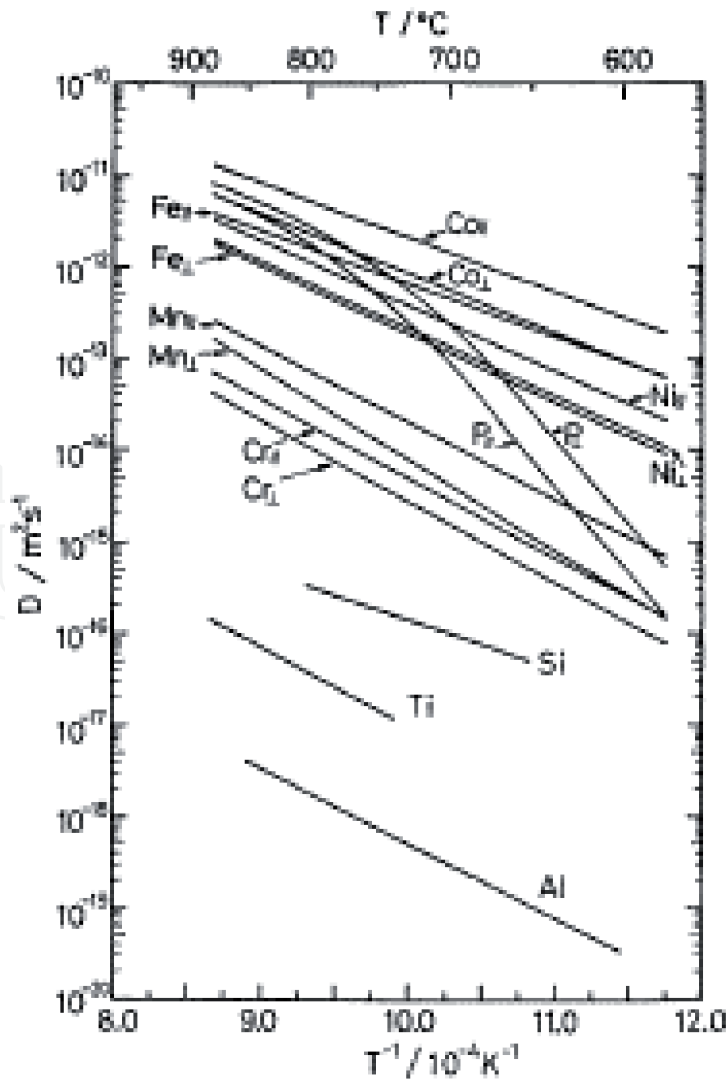


Figure 6.
Temperature dependence of self- and temperature diffusivity in β type titanium alloy (as called from [33]).

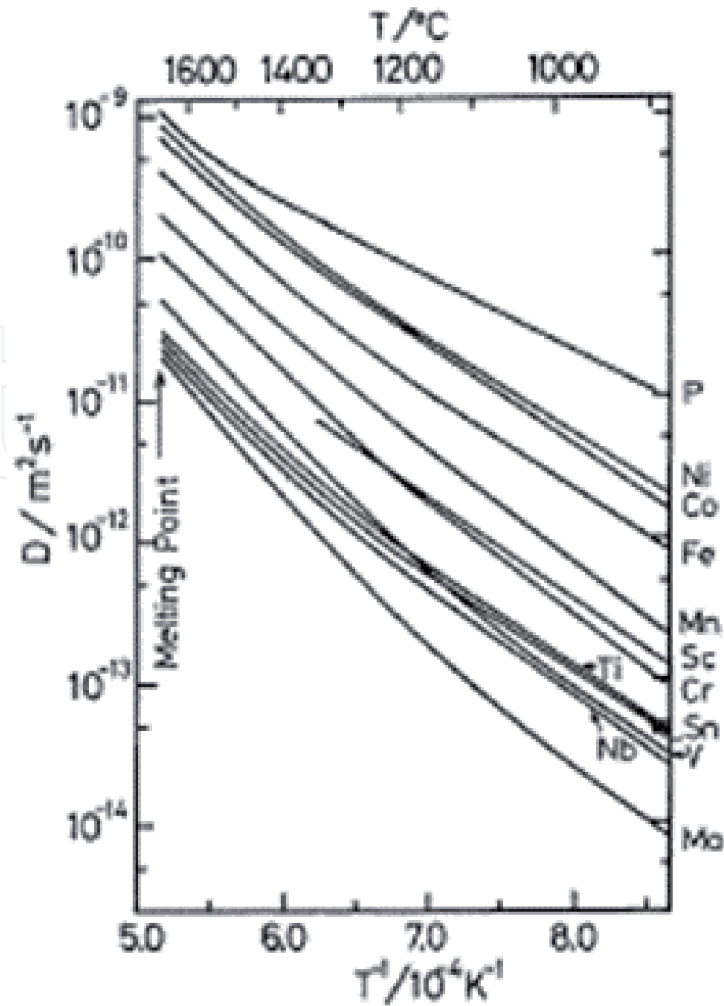


Figure 7. Temperature dependence of impurity diffusion coefficient in α titanium: Co, Fe, Ni, Mn, Cr and P in single crystal and Si, Al and Ti in polycrystal, culled from [33].

Al and Mo are shown as examples of slow diffusing elements from the group of slow diffusing elements, Others includes the other alloying elements, such as, V and Sn, which are close to Al and Mo. Element Fe is shown as an example in the group of fast diffusing elements in the figure. However, Ni is slightly faster, whereas Cr and Mn fall in between Fe and the β Ti-self-diffusion line.

Subsequently systematic measurements were hitherto made for the diffusion of Fe [51] Ni, [52] Mn, [53] Cr [54] and P [55]. On the other hand, Raiszinen and Keinonen measured diffusivities of Al [56] and Si [56] in polycrystalline Ti by a nuclear-reaction method. A detailed analysis of the data is compiled in the form of Arrhenius plots in the review by [57] and presented in **Figure 7**. The findings has shown that transition metal elements and phosphorus exhibit fast diffusion, which are three to five orders of magnitude faster than the self-diffusion. While, measurements done on ultrahigh purity α titanium with respect to Fe, Ni, and Co impurities resulted in very low diffusivity rates for self-diffusion in titanium and about two orders of magnitude slower than Fe, Co, and Ni [58].

5. Self-healing concepts in titanium based materials

It is well known that research in the field metallic self-healing is still in its infancy stage. Self-healing metallic materials has received attention only in the past decade [13, 18]. While previous reviews on self-healing materials [59] have focused

on describing the various routes to obtain self-healing mostly in polymeric materials, the present chapter is directed toward physical or chemical mechanism can be used to engineer self-healing in Ti-metals and its alloys.

5.1 Electrochemically induced self-healing

Self-healing coatings inspired by biological systems possess the ability to repair physical damage or recover functional performance with minimal or no intervention. When the kinetics are extremely fast, the phenomenon is controlled by the diffusion (mass transport) of the species that enters or leaves the surface of the material under consideration. Consequently, the composition of the system will also be changing. Analogous effects have been found by other workers in systems of biological interest, e.g., with processes involving membranes and enzymes. It is well known that the basic diffusion controlled modes, such as surface diffusion, D_s ; grain boundary diffusion, D_{gb} ; vacancy diffusion, D_v and pipe diffusion, D_p , are fundamental to determine the rate of atomic diffusion in polycrystalline metals. In general, surface diffusion occurs much faster than grain boundary diffusion, and grain boundary diffusion occurs much faster than lattice diffusion. Atomic diffusion and indeed electrochemical-induced self-healing in polycrystalline materials is therefore often modelled using a combination of diffusion kinetics (see previous section). More details of the transformation modes in titanium have been discussed elsewhere [31–33]. For this, electrochemically induced self-healing are said to be a good strategy to be exploited in metals. For instance, a damage to oxide films, which normally protect the surfaces of Ti materials from corrosion, can be repaired by reoxidation in air. Recently, Gang Lu et al. [60] studied the oxidation of a polycrystalline titanium surface by oxygen and water and found that at 150 K O_2 can oxidize Ti to Ti_5 , Ti_3 and Ti_2 , while exposure of Ti to H_2O at this temperatures only produces Ti_2 species. At temperatures above 300 K, H_2O can by both O_2 and H_2O slightly increases a further oxidize Ti_2 to higher oxidation states. They observed rising temperature promotes the diffusion of oxygen into the bulk of the sample, which increasing overall oxidation. This is because the thickness of the oxide coating on Ti surface depends on both the duration of O_2 exposure and on the sample temperature. At a given temperature, Ti oxidation by both O_2 and H_2O slightly increases as exposure increases.

Additionally, a crack on the surface of a titanium component can also be healed, when the oxidation reaction products fill up the crack cap. Therefore, cracks developed due to operational related stress can be autonomously self-healed or repaired by re-oxidative reaction that occur in Ti-based materials. Although self-healing coatings are considered as an alternative route for efficient anti-corrosion protection, intense research and development effort are been done in the area of corrosion protection coatings of metals and alloys. However, in order to improve the equipment service prediction capabilities of infrastructure, the use of Ti-based materials in infrastructures are beneficial as it can act as a second line of safety assurance even after the coating has failed. In this context, autonomic healing materials respond without external intervention to environmental stimuli, and have great potential for advanced engineering systems [61]. However, the limitation of this self-healing approach is that the extent of oxidation depends on sample temperature. A recent study identified 550–600 K as maximum oxidation in Ti based alloy. Upon heating the oxidized Ti above 850 K the titanium oxide layer is completely reduced to Ti^0 , which is effective.

5.2 Thermally activated solid phase healing in titanium

This mechanism is based on a thermoelastic displacive phase transformation design methodology. Certain strongly ordered intermetallic systems exhibit

shear-dominated thermoelastic displacive transformations that involve minimal volume dilatation, a high degree of crystallographic reversibility, and a low-temperature allotrope that readily twins during plastic deformation. This combination gives rise to the well-known shape-memory effect in which plastic deformation imparted to the low-temperature martensitic phase can be reversed almost completely during transformation to the high-temperature austenitic phase.

In a recently study, by Elena et al. [62] thermally engineered self-healing was proven by observation of crack healing after annealing. Microscopic deformation and recovery of a shape-memory nickel-titanium alloy were studied. The deformation was induced by microindentation using spherical and Vickers diamond indenters. The recovery of the indents, caused by thermal annealing, was measured quantitatively using an optical surface profiler. Microindents formed by a spherical diamond in an equiatomic nickel-titanium martensite almost completely recover at low indentation load when moderately heated [63]. A smaller recovery ratio was observed for microindents formed by Vickers indenters. These observations suggest that the shape-memory effect exists at the microscopic level and under complex loading conditions. The observations were rationalized using the concept of representative strain and maximum stress under the spherical and pyramidal indenters. A representative surface profiles measured before and after heating for both spherical and Vickers indents are shown in **Figure 8(a)** and **(b)**, respectively. The degree of indent recovery was determined quantitatively from the surface profiles by defining a recovery ratio, d , as.

5.3 Precipitation in under-aged alloys

This is an approach, of self “healing” is likened to an established metallurgical process of aging. In this mechanism, a defect sites (primarily microscopic voids) serve as nucleation centers for diffusion driven precipitation of oversaturated

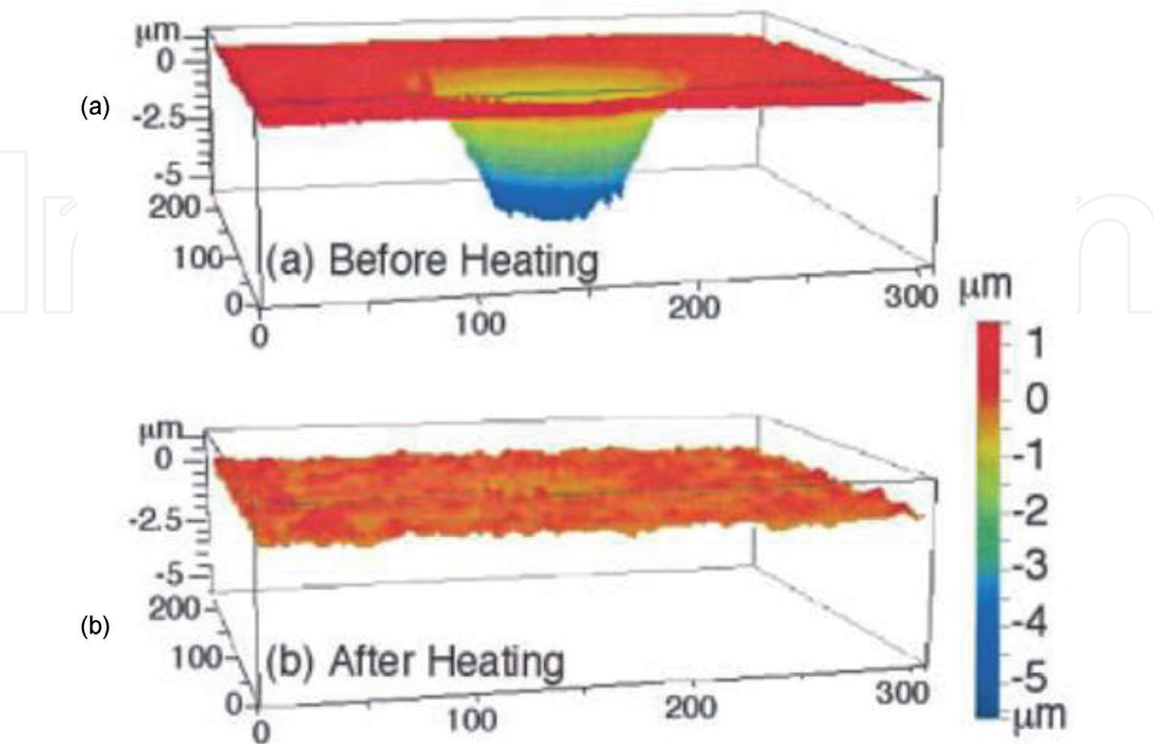


Figure 8.
A representative three-dimensional profile of a spherical indent at load of 15 N: (a) fresh indent and (b) after heating above the austenite finish temperature.

solute in the alloy and are thereby immobilized from further growth until failure. Consequently, the newly formed voids are sealed before they grow and this results in improvement of creep and fatigue properties of the alloy. This form of 'preventive' healing has been used Al-Cu alloys, known for decreasing solute solubility with decreasing temperatures. The process involves a high-temperature solution treatment, accompanied by quenching and annealing for relatively short periods of time, results in an underage microstructure that maintains substantial amounts of solute and serves as the healing agent. The processes of "secondary precipitation" in Al-Cu alloys that results into much finer precipitates from low-temperature aging [64] and investigations into dynamic precipitation in Al-Cu-Mg-Ag alloys occurring in response to moving dislocation generation under load [65], have been identified as potential healing mechanisms during fatigue and creep. This can be extended to other metallic materials. The limitation to this approach is that not all Ti alloy is heat treatable like Al-Cu alloys.

5.4 Micro-encapsulated low-melting healing agent reinforced metal matrix composites (MMCs)

This technique derives its inspiration from polymer healing and was recently conceptualized by Rohatgi et al. [63] includes the embedding of a hollow reinforcement (micro-sphere, micro-tube) containing a low-melting alloy in a higher melting metal matrix. The encapsulation of a metallic healing agent, however, allows the microcapsule to serve as a diffusion barrier and the interface should be sufficiently fragile to break upon an advancing crack and not deflect.

In the line of work done on hollow fibers reinforced polymers [66], attempts were also made to integrate hollow microfibers containing low-melting healing agents into metallic systems [67]. This attempted healing was implemented by incorporating indium as a healing agent in carbon tubes embedded in a higher melting solder matrix. Upon heating beyond the Indium melting point, a macroscopic crack that was directed downward to gravity was repaired. Computational fluid dynamics studies were conducted by Lucci et al. [67] on this healing method and interface wettability and gravity-related crack orientation were highlighted as major factors affecting the flow of healing liquid, with more wetting systems and gravity-oriented cracks being more desirable to fill.

5.5 Shape memory alloy (SMA) reinforced metal matrix composites (MMCs)

In one of the earliest trial, Manuel and co-workers [68] used this approach to heal Sn and Mg based metallic materials. The method involves reinforcing an alloy matrix with wires made of a shape-memory alloy (SMA), such as nitinol (NiTi). SMA wires have the ability to recover their original shape when heated above a critical temperature [69]. Thus, when the metal matrix composite cracks, the resulting plastic strain stretches the SMA that bridges the crack. On heating above the shape transformation temperature of the SMA, the wire shrinks back to its original shape applying compressive force to the matrix and clamping the crack. This is accompanied by welding of the crack in the matrix alloy which is so-designed as to partially liquefy at the healing temperature [70].

6. Summary

Although the production of autonomous self-healing in metallic materials has been the subject of numerous studies and will continue to be in the near future.

It is still at the infancy stage. Thus far, the field of autonomous self-healing engineering materials has been dominated by polymeric based substances for several years with only one route and mechanism, that of the encapsulated liquid adhesive route. The current chapter discusses the framework for engineered self-healing Ti-alloys has been presented with some practical examples revealing how self-healing functionality can be incorporated in Ti alloys. Nonetheless, the functionality of the mechanism comes down to the turning these experimental approaches under laboratory conditions into commercially available materials and products. Albeit, the studies conducted thus far in Ti and indeed metals have been relatively limited, the information contained within this chapter should not be considered exhaustive, and should be open to further improvement, modification and discussion. There are obvious indications that, the once impossible task of achieving autonomously engineered self-healing metallic materials in service will be feasible in no distant time.

Author details

Paul Sunday Nnamchi^{1,2,3*} and Camillus Sunday Obayi¹

¹ Department of Metallurgical and Materials Engineering, University of Nigeria, Nsukka, Enugu State, Nigeria

² Department of Mechanical and Construction Engineering, Wynne Jones Building, Northumbria University, Newcastle upon Tyne, United Kingdom

³ Department of Metallurgical and Materials Engineering, Enugu State University of Science and Technology, Agbani, Enugu State, Nigeria

*Address all correspondence to: paul.nnamchi@esut.edu.ng;
paul.nnamchi@northumbria.ac.uk

IntechOpen

© 2020 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Alaneme KK, Bodunrin MO. Self-healing using metallic material systems—A review. *Applied Materials Today*. 2017;**6**:9-15
- [2] Martin P. Wound healing—Aiming for perfect skin regeneration. *Science*. 4 Apr 1997;**276**(5309):75-81
- [3] Trask RS, Williams HR, Bond IP. Self-healing polymer composites: Mimicking nature to enhance performance. *Bioinspiration & Biomimetics*. 2007;**2**(1):1
- [4] Van Tittelboom K, De Belie N. Self-healing in cementitious materials—A review. *Materials*. 2013;**6**:2182-2217
- [5] Shi S-C, Huang T-F. Self-healing materials for ecotribology. *Materials*. 2017;**10**:91
- [6] Gupta RK, Mirza F, Khan MUF, Esquivel J. Aluminum containing Na_2CrO_4 : Inhibitor release on demand. *Materials Letters*. 2017;**205**:194-197
- [7] Fan Z, Wang K, Dong X, Wang R, Duan W, Mei X, et al. Enhanced cyclic oxidation resistance through the self-healing of segmented cracks using nano- Al_2O_3 /Ni-20 wt% Al particles in laser re-melted thermal barrier coatings. *Materials Letters*. 2017;**201**:156-160
- [8] Du K, Guo X, Guo Q, Wang F, Tian Y. A monolayer PEO coating on 2024 Al alloy by transient self-feedback control mode. *Materials Letters*. 2013;**(91)**:45-49
- [9] Zhang Y, Li Y, Ren Y, Wang H, Chen F. Double-doped LDH films on aluminum alloys for active protection. *Materials Letters*. 2017;**192**:33-35
- [10] Rohatgi PK. Al-shape memory alloy self-healing metal matrix composite. *Materials Science and Engineering A*. 2014;**619**:73-76
- [11] Grabowski B, Cem T. Self-healing metals. In: *Advances in Polymer Science*. New York, NY, USA: Springer; 2015
- [12] Li W, Jiang Z, Yang Z. Extension and possibility of debonding in encapsulation-based self-healing materials. *Materials*. 2017;**10**:589
- [13] Kim D-M, Cho Y-J, Choi J-Y, Kim B-J, Jin S-W, Chung C-M. Low-temperature self-healing of a microcapsule-type protective coating. *Materials*. 2017;**10**:1079-1093
- [14] Hautakangas S, Schut H, van Dijk NH, Rivera Diaz del Castillo PEJ, van der Zwaak S. Self-healing of deformation damage in underaged Al-Cu-Mg alloys. *Scripta Materialia*. 2008;**58**:719-722
- [15] Sheng X, Lei Q, Xiao Z, Wang M. Precipitation behavior and quenching sensitivity of a spray deposited Al-Zn-Mg-Cu-Zr alloy. *Materials*. 2017;**10**:1100
- [16] Hastings GW, Mahmud FA. Intelligent orthopaedic materials. *Journal of Intelligent Material Systems and Structures*. 1 Oct 1993. pp. 452-456
- [17] Varley RJ, van der Zwaag S. Towards an understanding of thermally activated self-healing of an ionomer system during ballistic penetration. *Acta Materialia*. 2008;**56**(19):5737
- [18] Hanson BH. Present and future uses of titanium uses in engineering. *Materials and Design*. 1986;**7**:301-307
- [19] Klinger MM, Rahemtulla F, Prince CW, Lucas LC, Lemons JE. Proteoglycans at the bone-implant interface. *Critical Reviews in Oral Biology and Medicine*. 1998;**9**:449
- [20] Collings EW, Gegel HL. A physical basis for solid solution strengthening and phase stability in alloys of titanium. *Scripta Metallurgica*. 1973;**7**:437-443

- [21] Welsch G, Boyer RR, Collings EW. *Materials Properties Handbook: Titanium Alloys*, ASM Handbook. USA: Institute of Metals; 1994
- [22] Newkirk JB, Geyser AH. Crystallographic aspects of beta to alpha transformation in titanium. *Acta Metallurgica*. 1953;1:370
- [23] Oka M, Taniguchi Y. {332} diffusion twins in a Ti-15.5 pct V alloy. *Metallurgical and Materials Transactions*. 1979;10A:651
- [24] Collings EW, Ho JC, Jaffee RI. Superconducting transition temperature, lattice instability and electron-to-atom ratio of transition-metal binary solid solutions. *Physics Review*. 1972;5:4435-4449
- [25] Burgers WG. On the process of transition of the cubic-body-centered modification into the hexagonal-close-packed modification of zirconium. *Physica*. 1934;1:561-586
- [26] Blanco MA, Francisco E, Luaña V. GIBBS: Isothermal-isobaric thermodynamics of solids from energy curves using a quasi-harmonic Debye model. *Computer Physics Communications*. 2004;158:57-72
- [27] Reedhill RE, Abbaschian R. *Physical metallurgy principles*. In: The Pws-Kent Series in Engineering. United Kingdom: Cengage Learning; 1991
- [28] Hirao M, Ogi H, Kai S, Ledbetter H, Tarumi R, Takashima K. Titanium's high temperature elastic constants through the hcp-bcc phase transformation. *Acta Metallurgica*. 2004;52:2075-2080
- [29] Deurig TW, Williams JC. Beta Titanium Alloys in the 1980s. In: Boyer RR, Rosenberg HW, editors. *New York, USA: AIME*; 1984. pp. 19-67
- [30] Burgers WG. On the process of transformation of the cubic body centered modification into hexagonal close packed modification in zirconium. *Physica*. 1934:561-586
- [31] Banerjee D, Muraleedharan K. Substructure in titanium alloy martensite. *Philosophical Magazine A*. 1998;77(2):299-323
- [32] Paul S. Nnamchi. Published thesis presented for the award of PhD. United Kingdom: University of Sheffield; 2014; p. 127
- [33] Liu Z, Welsch G. *Materials Transactions*. 1988;19A:121
- [34] Jepson KS, Brown ARG, Gray JA. In: Jaffee RI, Promisel WE, editors. *Proceedings of the First International Conference on Titanium*. London: Pergamon; 1970. p. 677
- [35] Furuya Y, Shimada H. Shape memory actuators for robotic applications. *Materials and Design*. 1991;1(12):21-28
- [36] Petrini L, Migliavacca F. Biomedical applications of shape memory alloys. *Journal of Metallurgy*. 2011;2011:1-15. DOI: 10.1155/2011/501483
- [37] Lieva VL, Carla H. Smart clothing: A new life. *International Journal of Clothing Science and Technology*. 2004;16:63-72. DOI: 10.1108/09556220410520360
- [38] Cayton C. Shifting the shear paradigm in the crystallographic models of displacive transformations in metals and alloys. *Crystals*. 2018;8(4):181. DOI: 10.3390/cryst8040181
- [39] Nnamchi P, Younes A, González S. A review on shape memory metallic alloys and their critical stress for twinning. *Intermetallics*. 2019;105:61-78
- [40] O'Brien B, Weafer FM, Bruzzi MS. Shape memory alloys for use in medicine. In: *Reference Module*

in Materials Science and Materials Engineering. Elsevier; 2017

[41] Buehler WJ, Gilfrich J, Wiley R. Effect of low-temperature phase changes on the mechanical properties of alloys near composition TiNi. *Journal of Applied Physics*. 1963;**34**:1475-1477

[42] Stoeckel D. Shape memory actuators for automotive applications. *Materials and Design*. 1990;**11**:302-307. DOI: 10.1016/0261-3069(90)90013-A

[43] Bellini A, Colli M, Dragoni E. Mechatronic design of a shape memory alloy actuator for automotive tumble flaps: A case study. *IEEE Transactions on Industrial Electronics*. 2009;**56**:2644-2656

[44] Hartl DJ, Lagoudas DC. Aerospace applications of shape memory alloys. *Proceedings of the Institution of Mechanical Engineers, Part G: Journal of Aerospace Engineering*. 2007;**221**:535-552. DOI: 10.1243/09544100JAERO211

[45] Fujita H, Toshiyoshi H. Micro actuators and their applications. *Microelectronics Journal*. 1998;**29**:637-640. DOI: 10.1016/S0026-2692(98)00027-5

[46] Valiev RZ, Islamgaliev RK, Alexandrov IV. Bulk nanostructured materials from severe plastic deformation. *Progress in Materials Science*. 2000;**45**:103-108

[47] Rogers HC, Hirth JP, Reed-Hill RE. *Deformation Twinning*; Proceedings. New York: Gordon and Breach Science Publishers; 1964

[48] Zhu Y, Liao X, Wu X. Deformation twinning in nanocrystalline materials. *Progress in Materials Science*. 2012;**57**:1-62

[49] Wang J, Zeng Z, Weinberger CR, Zhang Z, Zhu T, Mao SX. In situ atomic-scale observation of

twinning-dominated deformation in nanoscale body-centred cubic tungsten. *Nature Materials*. 2015;**14**:594-600

[50] Zwicker U. *Titan and Titanlegierungen*. Berlin, Germany: Springer-Verlag; 1974. p. 102

[51] Perez RA, Nakajima H, Dymont F. Diffusion in α -Ti and Zr. *Materials Transactions*. 2003;**44**(1):2-13

[52] Nakamura Y, Nakajima H, Ishioka S, Koiwa M. Effect of oxygen on diffusion of manganese in α -titanium. *Acta Materialia*. 1988;**36**:2787

[53] Nakamura Y, Nakajima H, Ishioka S, Koiwa M. Effect of oxygen on diffusion of manganese in α -titanium. *Acta Metallurgica*. 1988;**36**:2787

[54] Nakajima H, Ogasawara K, Yamaguchi S, Koiwa M. Diffusion of chromium in α -titanium and its alloys. *Materials Transactions, JIM*. 1990;**31**:249

[55] Nakajima H, Nakazawa J, Minonishi Y, Koiwa M. Diffusion in titanium. *Philosophical Magazine*. 1986;**A53**:427

[56] Raisnen J, Anttila A, Keinonen J. Diffusion of aluminum in ion-implanted α -Ti. *Journal of Applied Physics*. 1985;**57**:613

[57] Nakajima H, Koiwa M. Diffusion in titanium. *ISIJ International*. 1991;**31**:757-766

[58] Mishin Y, Hertig C. Diffusion in the Ti-Al system. *Acta Materialia*. 2000;**48**:589

[59] Sharma S et al. Recent advances in self-healing. *Materials Today: Proceedings*. 2019;**18**:4729-4737

[60] Lu G, Bernasek SL, Schwartz J. Oxidation of a polycrystalline titanium

surface by oxygen and water. Surface Science. 2000;**458**:80-90

[61] Kamat S, Su X, Ballarini R, Heuer AH. Structural basis for the fracture toughness of the shell of the conch *Strombus gigas*. Nature. 2000;**405**(6790):1036

[62] Lumley RN, Polmear LJ, Morton AJ. Interrupted aging and secondary precipitation in aluminum alloys. Materials Science and Technology. 2003;**19**:1483-1490

[63] Rohatgi PK. Self-Healing Metals and Alloys-Including Structural Alloys and Self-healing Solders. U.S. Patent Application 12/537, 675; 2009

[64] Lumley RN, Polmear LJ, Morton AJ. Interrupted aging and secondary precipitation in aluminum alloys. Materials Science and Technology. 2003;**19**:1483-1490

[65] Hautakangas S, Schut H, van der Zwaag S, del Castillo PEJRD, van Dijk NH. Positron annihilation spectroscopy as a tool to develop self-healing in aluminum alloys. Physica Status Solidi. 2007;**4**:3469-3472

[66] Trask RS, Bond IP. Biomimetic self-healing of advanced composite structures using hollow glass fibers. Smart Materials and Structures. 2006;**15**(3):704-710

[67] Lucci JM, Ruzek A, Misra SK, Rohatgi PK, Amano R. Self-healing in metal castings. In: Proceedings of American Foundry Society. Illinois, USA: Schaumburg; 2011

[68] Manuel M, Olson GB. Biologically inspired self-healing metals. In: Proceedings of the 2nd International Conference on Self-Healing Materials. Chicago; 2009

[69] Feng QL, Cui FZ, Pu G, Wang RZ, Li HD. Crystal orientation, toughening

mechanisms and a mimic of nacre. Materials Science and Engineering: C. 2000;**11**:19-25

[70] Lumley RN, Morton AJ, Polmear LJ. Enhanced creep performance in an Al-Cu-Mg-Ag alloy through underageing. Acta Materialia. 2002;**50**:3597-3608