

Design and Development of Self-Healing Coating

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Abstract— Self-healing materials are inspired by the several biological phenomena seen in organisms that have capability to heal themselves by themselves are catching attention in recent years. Most researchers have already focused on different types of self-healing material like concretes, ceramics and polymers. It is seen that the self-healing metallic materials has a certain task which is challenging and this is due to the high temperatures used in manufacturing. To know about the self-healing technique, it a method of repairing the damaged area of the base material or a specimen through certain methods. There are different kinds of self-healing process that will be shown in the upcoming data but the main technique that comes in play is self-healing material coating method. In this method there will be coating two kinds of metal on the specimen base material i.e., first, need to know the ratio of both metal for doing the coating in which is taken 60% part of the alloy is Indium and the other 40% is Tin and the technique it is using for the coating the In-Sn alloy is by flame coating method. Apart from that the process of the self-healing works in case of coating based self-healing, first when there is a wear or any kind of damage in the base material then the coated metal will reach to its melting point temperature and due to this the portion of the alloy settles into the crack or wear area which solidifies after some time but it is seen that some change in some mechanical properties. It showed that fatigue crack growth which have a low crack-tip driving force that will get restricted after the self-healing process, and it is observed that the crack growth rate which happened due to higher crack-tip driving force. Knowing that the challenge comes in when it comes to the high temperature that is required in manufacturing and other chemistries involved when it comes to self-healing metallic materials. This article summarizes and evaluates the different types of the self-healing mechanisms used in metallic materials and reviews on different types of experiment done and the output received from the data of different alloys and generalization of the process involved in different types of self-healing of a metallic material.

Index Terms: Self-healing process, self-healing metallic materials, flame coating method.

I. INTRODUCTION

Self-Healing material coating is needed to be done if we need to enhance the intrinsic properties on the surface of the base metal, metallic type of self-healing coating will increase the life of the material and also minimize the maintenance and maximize the cost efficiency by not only healing the damage area by the surface properties of the self-healing material but also gives better protection against corrosion and reduce visible damage on the surface. Engineering materials is degrading due to certain conditions like wear, fatigue, creep, and other environmental conditions and these are limiting their life and this can result into catastrophic situations. To improve quality and life of these materials, new type of materials needed to be developed that can provide a resolution to this type of problem so that it can be used not only in automotive sector but also in aerospace, civil, and biomedical sectors. So, for this Self-healing materials comes in the play, they are the kind of materials that have the ability to self-heal or repair themselves from damage that gives us effective solution. Self-healing materials is highlighted as the smart materials, which can repair partly or all the certain mechanical properties and functions of the material after it takes damage. Mostly these materials classified into two categories, one is extrinsic type of self-healing materials and second is intrinsic type of self-healing materials. But there is a limitation of extrinsic self-healing materials and that is they can be healed certain number of times which we see over the past decade and due to this limitation, many intrinsic self-healing materials have been used by employing by two kind of bonds that is dynamic covalent bonds or non-covalent bonds in which interactions that can be root out and reconstructed after if there is breaking occurred. Apart from that to create the self-healing materials metallic based is a drudgery and this is because of the high melting points of the metals, and we know that the repairing process can only take

place at higher temperature or in specified environmental conditions. Metallic based Self-healing often occurs at high temperatures as compared to polymer or ceramic self-healing systems. But apart from these difficult situations, there are some positive outcomes in the making or development of self-healing metals.

II. CLASSIFICATION OF SELF-HEALING METALLIC STRUCTURES

If we focus on classification of current self-healing metallic materials which focuses on the technique/mechanisms of self-healing, based on structure of the material or their autonomy. But the nonautonomous self-healing materials will require additional actuation for instance the application of heat or an electrical current but in case of autonomous self-healing materials they do not require any kind of external factor, but as far as we know accordingly to this time the autonomous metallic self-healing structures are majorly theoretical without any significant practically experimental implementation. Self-healing metallic material coatings have a homogeneous structure which is macroscopic which includes the shape memory alloy (SMA) fibres which also consists of healing agents merged in the matrix. Whether it is long shape memory alloy wires or short they both have been implanted as reinforcements towards today's advancements in metal matrixes (such as Al, Zn, Sn, Sn-Bi, or In-Sn alloy) to synthesize shape memory alloy based self-healing materials [1-6]. Self-healing materials are based on healing agents which are synthesized by adding the capsules or tubes that is containing a healing agent like a solder [7-12]. Self-healing metals are more homogenous and they are consisting healing mechanisms that is also including some healing methods such as coating-based healing [13], electro-healing [14] method, eutectic-based technique, and healing based on precipitation [15-21], which will be elaborated in detail in the upcoming sections.

III. SELF-HEALING MECHANISMS

A. HEALING BASED ON PRECIPITATION METHOD

In precipitation hardening alloy decrease in solubility of the solute element will occur with decrease in temperature. Therefore, during the phase of solidification, the alloy will be changing its form from liquid to a single solid state and after that single solid phase will change into two solid phases after solidification. If we reheat the two-phase solid to a certain temperature at which it will go back to the single-phase material which is stable, this can make the material enter a state of metastable when quenched or cooled down rapidly while the alloy is at high temperature and the alloy is in supersaturated state with solute at that temperature. Subsequently precipitation heat treatment method are conducted at lesser temperatures at which the two-phase solid remain stable and that will result in solute precipitation and this is obtained by three different stages or condition of material and the conditions are: First condition is underaged—profuse and finely precipitates coherently with the matrix, then second is peak-aged-precipitates bordering on incoherency, and last condition is overaged—which is fewer and the coarse precipitates incoherently with the matrix. While the alloy precipitates it tends to form a region of high-stress or high-energy region such as voids/empty space and also forms the areas of high dislocation density. Now, dislocations and voids majorly tend to concentrate at high stress regions which will be eventually causing cracks. Due to the precipitate nucleation the growth can be seen most probably in these regions and the crack growth can be reduced or override to a degree that will be providing some measure of healing. For instance, in case of open-volume defects, such as presence of void, vacancy clusters, and dislocations these facilitates the diffusion of solutes and hence increase the rate of precipitation, and this will be going to promote the self-healing of metals by the dynamic precipitation. And by this crack growth can be retarded/decreased or reversed. It is seen that while the process of healing of an aluminium and copper alloy which went to heat treatments after being underaged so that it can be tested in such a way as the crack is produced. It is reported that if creep damage is seen in austenitic stainless steel, it can be healed which is containing boron and copper and it can be done by dynamic precipitation from the supersaturated matrix of all these elements and the creep resistance was

seen to be improving when we precipitate partially filled nanoscale to the

Figure 1. [28], Figure 2. [29]

Fig. 1. Micrographs of an Al-Cu AA2001 alloy specimen undamaged at 160°C for 5 h and tested. (a) Hairline crack present and (b) crack has been healed by aging for an additional 10 h.

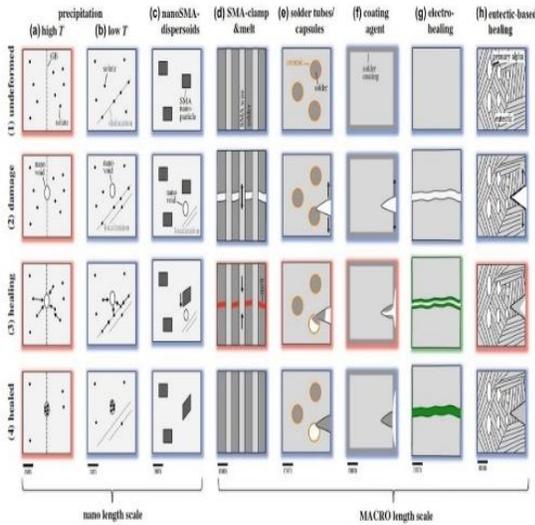


Fig. 2. Schematic representation of the self-healing mechanisms in metallic materials: (a) high-temperature precipitation-based healing, (b) low-temperature precipitation-based healing, (c) nano-SMA-dispersoids-based healing, (d) SMA-based healing, (e) microencapsulation-based (microballoons/microcapsules/microtubes) healing, (f) coating-based healing, (g) electro-heating, and (h) eutectic-based healing. Background shading indicates the conditions required: red = high temperature, blue = low temperature, and green = applied voltage. Reprinted with permission.

open volume of defective area and therefore prevented any other state of damage. On comparison of the precipitation kinetics in deformed alloys like Fe-Cu and Fe-Cu-B-N alloys by the method of positron annihilation spectroscopy their outcome will be shown that the open-volume defects caused by the plastic deformation is in the form of pure iron (Fe) and can be recovered successfully by the self-diffusion of iron (Fe) atoms during the process of aging and this kind of behaviour is not depending on the heat treatment before testing. During the tests on Fe-Cu alloy indicates that copper precipitation is caused by the presence of dislocations. It is seen that due to the properties of the different types of alloys, self-healing of the Fe-Cu-B-N alloys will be going to take place as B-N precipitates, followed by copper precipitation if there is a large creep cavity.

B. SHAPE MEMORY ALLOY-BASED HEALING

In this method the micro-size shape memory alloy (SMA) wires/fibres is pulled altogether at the location of the crack occurred and then the damaged surfaces is bonded together by using the technique of partial melting. These types of alloys are the

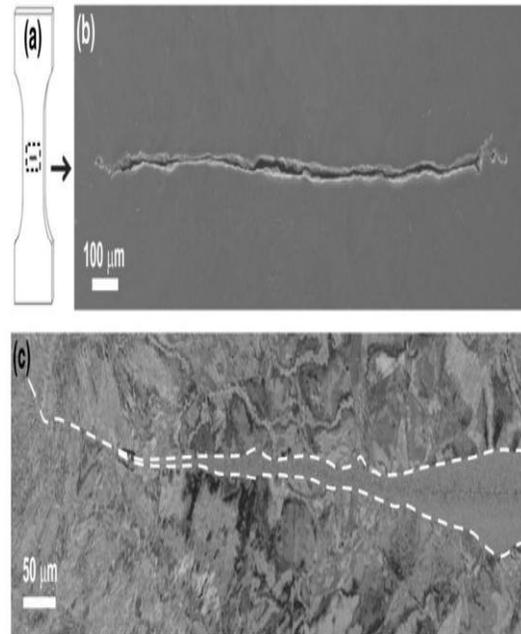
materials that will come back to its particular shape upon which the application of heat is applied and this will change the phase including the other two phases known as austenite and martensite. Shape Memory Alloys are transformed by the change from martensite to the austenite phase on heating, and when cooled it will go back to the martensite phase. The SMA can be easily deformed in the martensite state, by responding to stress by changing the positioning of its crystal structure [22][23]. During the self-healing condition, SMA wires that are embedded in a metallic system will get reverse from martensite to austenite under heating condition to achieve crack repairing. If the wires implanted in the sample material have been pretrained, then the damaged material will be experiencing a clamping force that is exerted on it. Usually, the matrix materials that are used in these types of systems is found to be off-eutectic alloys. Off-eutectic alloys are those who have different solid and liquid temperatures, and in between these temperatures, this type of alloy exists as semisolid state and the solid particles of semisolid paste is surrounded by the molten liquid which is supposed to be higher than the certain temperature. The quantity of material in molten state can be controlled by heating to desired temperature. Tin and bismuth are one of the examples of eutectic alloy which have a low melting point near about 139 degrees Celsius. If we take a damaged sample to be healed in such state at which temperature of the system is reached at a point at which SMA wires will start rearranging its original configuration, and then bind the damaged surfaces together. As the temperature of healing is between the solid and liquid temperatures, the material partially melts that will be having enough material solid that can maintain the structural integrity of the system. The liquid remained at every surface can flow or they can fill the gap created at the damage area and after cooling it resolidify and thus this the way it heals the system. If we fabricate a Tin-based self-healing composite using a Tin matrix and SMA wires. In such case the SMA wire bracing are continuously and uniaxially aligned in the matrix. And the wires were coated with gold to enhance the wettability surface of the wire. When tensile tests were performed to check out the mechanical outcome of the composite and matrix alloys it was seen that the composite displayed increase in uniform ductility

in comparison of the unreinforced sample coating material and this is because of toughening of composite which improve the attributed grain refinement of the alloy because of the presence of the Shaped Memory Alloy and the interfacial debonding or filling up the crack at the interference of the matrix. If we take the healing efficiency in mind, we need to perform tensile tests on the composites at room temperature until there is the matrix fail completely. Once the material fails, remove the specimens from the tensile testing apparatus and keep it under heat-treatment condition to heal the crack. Once the crack is healed, then again put the specimens under the tensile test for the failure one more time to determine the amount of recovery of strength, which turned out to be more than that of the original composite ultimate tensile strength, but there was reduction seen in the uniform ductility which is attributed to defects submitted at the crack surface area during healing while including the oxides, voids, and brittle eutectic phases. If SMA works on Sn-Bi alloys which has magnesium-based cast alloy, it has a high specific strength and we can see the increase in uniform ductility which resulted in composite toughening. So, it is found out that as the SMA wires closes the crack, rough surface of crack walls came into play and prevented the complete closure of the specimen. But in Mg-based alloy the force applied by the SMA wires overcome the matrix strength of Sn-Bi matrix composite. Performance of the composite can be seen at that interference which is turned to having a low strength and reinforcement due to poor wetting.

C.COMPOSITE MATERIALS REINFORCED WITH A HEALING AGENT

When it comes to self-healing composite, we can see that after it get synthesised by effect of low melting temperature to the alloy that is subjected to the damaged are and this will act as a healing agent while being in high-melting temperature of the alloy metal matrix composite [24-27]. If we consider a composite that is having an Aluminium alloy whose matrix is meshed with hollow ceramic tubes in which the empty spaces are infiltrated under the low melting temperature of Tin and Lead solder. In ordered to check the results, a hole was drilled to the material in order to simulate the crack in the metal matrix that is moving into the microtube after that the sample alloy

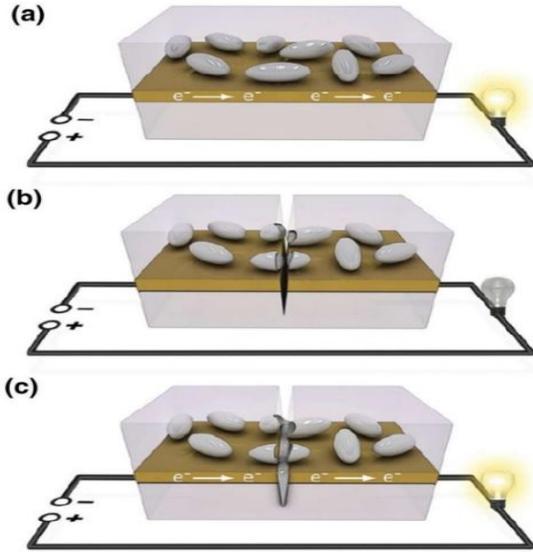
was subjected to heat treatment above its melting point and after that the temperature is reduced to room temperature after a small interval of time.



(a) Location of crack in tensile sample, (b) crack in Ni before healing, and (c) healed crack.

When we do this, we can see that we observed that the solder that we used overflowed from the microtubes in order to seal the effected or damaged area. The technique we using is having a drawback in which we see that there are only partial filled cracks, and high interfacial porosity is there between the bond of Aluminium and the solder, which reflects that interfacial bonding between the healing agent and the matrix is not up to the mark. If we see through fluid dynamic simulation, we can estimate the width and position of the crack that has to be healed. With the help of simulation, we can know the location of the healing agent where to flow into a crack measurement to the healing agent reservoir. To make a barrier between the low melting point metal and a higher melting point alloy during casting we need to encapsulate a low melting point metal in hollow microspheres. To ensure that cracks bridge through the wall material that is exposed to the healing agent for that we need proper diffusion barrier materials along with the low melting point metals, when they come in touch with each other the healing agent bonds with the matrix.

D. ELECTROCHEMICAL HEALING



Schematic of the self-healing process in solder employing liquid-metal-filled capsules.

Research shows that the electrochemical healing of Ni by using the electroplating method. In this they took purest polycrystalline Ni which already consist of cracks and the metal is cleaned by putting it into sulfuric or phosphoric acid and then it is subjected to various combinations of NiSO_4 , NiCl_2 , and HBO_3 which is a high throwing power plating solution in which electro-healing is done. And the healing temperatures will be changing according to the thickness of the metal and with increase in thickness the temperature required is also increasing. And after some time, it is seen that the healing material starts depositing epitaxially from each side of the crack and the crack starts filling with healing material. After the process it is noticed that the recovered strength is decreasing as soon as the thickness of the material is increasing and in the thickest samples it reached to the Ultimate Tensile Strength of the cracked samples metal but with this process, we can recover up to 96% of the original tensile strength. Apart from that the only limitation which can be see is that the electro-healing needs a medium i.e., the solution in which the material to be healed is submerged so this healing method is restricted to heal the specified size material.

E.SELF-HEALING SOLDER

If any conductor is broken then with the self-healing method, we can establish the electrical connection again by using the polymeric capsules that contains eutectic Ga-In alloy which is implanted on the solder.

When there is any kind of cracks that is formed in solder due to any kind of mechanical damage like fatigue cracks obtained from thermal cycling rupture, the alloy of Gallium and Indium liquid is to be flown into the affected area. When the atmospheric oxygen reacts with Ga-In it will be going to provide structural integrity to the healed area of the circuit. By this technique it was monitored that the recovery rate of pre-crack conductivity and to retain this conductivity for prolong interval of time is more than 99%. Even with the low concentration of the capsules the healing time period is still very decent.

F.EUTECTIC-BASED METHOD OF HEALING

In eutectic-based healing the solid dendritic phase maintained the structural integrity by the eutectic liquid that is formed within the solid as a healing phase. The desired way to use the composition of matrix alloy that is distant from the eutectic composition of a system, and this will result in forming dendrites of a phase at a higher temperature and eutectic. When the cooling occurs the dendrites of the primary phase will tend to form first from the melted part, this is because they have higher melting point. Remaining inter dendritic liquid will change the composition by those dendrites due to solute rejection that is pushing the composition of the inter dendritic liquid to the eutectic composition and thus it will be going to solidify between the dendrites. To initiate the process of self-healing, we need to see that the temperature of the system is increased to a certain point where the inter dendritic eutectic when melts start flowing to a crack in the sample which represent the healing phase, when the structural integrity of the system of the solid dendrites is maintained. The liquid eutectic is then available to flow between the dendrites into any cracks or voids that is present in the system. This liquid eutectic in the cracks will solidify during the cooling and this will initiate the healing of the system.

IV. COATING BASED SELF-HEALING

For the given self-healing method which is based on coating we taking two metals in consideration which is Indium and Tin. In which Indium have a melting point of 156 degrees Celsius and Tin have a melting point of 231.9 degree Celsius. For the coating the amount of both the metals required will be 60% of

indium and 40% tin (wt.%) and together there coating will be having a melting point of 124°C to a certain layer of thickness on the surface of a aluminium base metal. The coating will be done in such a way that the powdered form of both the metal will be coated by the method of flame coating. Once the coating is done then the base metal with coating subjected to the surface crack the system will be heated above the melting point of the In-Sn alloy which will initiate the filling of the crack by melting of the alloy in the aluminium specimen which is heated about 124°C. After the crack healing test we get that after the self-healing process the low crack-tip driving force could be arrested giving the rate of fatigue crack growth, and we get the result that there is reduction in crack growth rate that occurred at a higher crack-tip driving force.

V. CONCLUSION

Self-healing metallic material coating are healing critical points of macroscopic damage, which is like bone healing, that may require a certain step in healing and restoring it to its original geometry and keeping the joint position in exact shape along with healing. We can get the supply of information about the damage through Structural Health Monitoring (SHM), that is like the nervous system of the body who has the similar function like providing information about the location and seriousness of the damage, the triggers the process of healing mechanisms in a certain order and knowing the information about residual capabilities of the system before and after the healing process. SHM have a capability to tell the status after the healing process is done. Self-healing can lead certain change in behaviour that will make the fatigue life longer and also increases the safety along with lower maintenance costs, and several other desirable attributes that are required in building structures, biomedical implants, space structures, and transportation systems. In the Self-healing process of shape memory alloy fibres is been shown as low-melting alloys, that also includes Tin-based alloy and Aluminium alloys. We know that certain alloys have high temperature for melting so we need to develop new self-healing mechanisms for these types of alloys. If we consider the self-healing using micro balloons that contains the healing agents that is seen in Aluminium alloys and other solder alloys. Self-

healing is done by precipitation and diffusion healing of nanovoids and microcracks which is shown in Aluminium alloys and other alloys based on Nickel. We need to see that the healing of the metallic alloys that is autonomous since most of the techniques developed to require external triggering date including thermal or electric.

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