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Shape Memory Alloy Applications

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Charles Goodson Honors Program

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Introduction

Shape memory alloys (SMAs) are unique mixtures of metals that have qualities unlike any other substance. Most notably is their ability to "remember" a shape and revert back to that shape with the application of heat. One such alloy is the Ni-Ti alloy, Nitinol. SMAs also have many other favorable characteristics such as superelasticity, biocompatibility and much more. Superelasticity is the ability to bend under stress and then return to its original shape with the removal of the stressor. Biocompatibility means that the SMAs are not toxic to living organisms, whether they are only used periodically or left in permanently. Today they are used in everything from the Mars rover to dental wire. Since their discovery, SMAs have made a significant impact in engineering and medicine because of their unique properties. However, names such as shape memory alloys and Nitinol are still unknown to the general public who is unaware of their amazing potential in almost every facet of technology. Even engineering student researchers of the J.D. Patterson Summer Research Program did not learn about SMAs until they investigated them in their research during the summer of 2017. After much research, the power of this shape memory quality was harnessed to create a passive tracking model for the solar panel system that is now a charging station on campus. This project highlights the significance of SMAs and the need to promote their awareness. On top of that, the market for SMAs is astronomical and would be a worthwhile investment. The financial, medical, and mechanical importance of SMAs cannot be understated; therefore, they need to continue being pursued in both medical and nonmedical applications because their proven uses in the past and their incredible potential in the future.

The Shape Memory Effect

Figure 1. Phase change from austenite (left) to martensite phase (right) (Anadón, 2002).

The shape memory effect is due to the possession of two different molecular states in the solid form of the SMAs. Similar to how water has three characteristic phases, solid ice, liquid water, and gaseous water vapor, SMAs have two different phases. However, SMAs have different molecular phases within the same state of matter. The cooler phase is the martensite phase, which has a bent molecular structure, is more elastic, and can be bent into any shape. The hotter phase is the austenite phase, which has a cuboidal molecular structure, is rigid, and has a fixed shape (Figure 1). When heat is applied and there is a phase change, the SMA will stiffen into its rigid austenite shape, demonstrating this shape memory quality. The laws of thermodynamics govern the bond angles and the molecular phases of the SMAs. In cooler temperatures, the bent bond angles are more favorable than the cuboidal angles, resulting in the martensite phase. Then at higher temperatures, the right angles of the cuboidal molecular structure are favorable to the bent bond angles, resulting in the austenite phase.

Due to the thermodynamic preference for these specific molecular angles at their respective temperatures, there is a delay in the transformation from one phase to the next when going from hot to cold or cold to hot. This results in what is known as hysteresis in the SMAs, which means that the phase that the SMA is in at a temperature close to the transition temperature depends on the history of the SMA, or what state it was previously in before the temperature change began. For example, whenever a SMA is transforming from the martensite phase to the austenite phase, the SMA will stay in the colder martensite phase longer as the temperature increases until it reaches the end of the transformation temperature, where it will transform into the austenite phase.

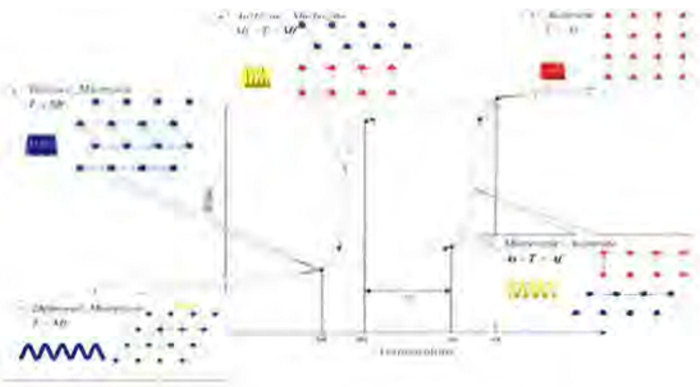

Figure 2. Temperature VS. Stress graph showing the transition temperatures(Anadón, 2002).

When phases of SMAs are graphed with temperature, a sigmoidal curve appears with a gap between the two curves, one that represents the transformation from cold to hot and then another that goes from hot to cold. The gap is due to hysteresis, and if this property were not present, then there would only be a single line on the graph. The reason that hysteresis exist in SMAs is that additional heat is needed to overcome the preexisting bonds that are preferable at that temperature. This hysteresis property means that the SMAs do not want to change their bond angles unless there is a considerable amount of energy poured into it. Similar to the mechanism of activation energy for an enzyme, there has to be enough heat being applied to the SMA before it will begin the process of changing its bond angles. There is not a proportional change to the bond angles with the transition temperatures - the SMAs either want to be bent or square, not in between (Figure 2).

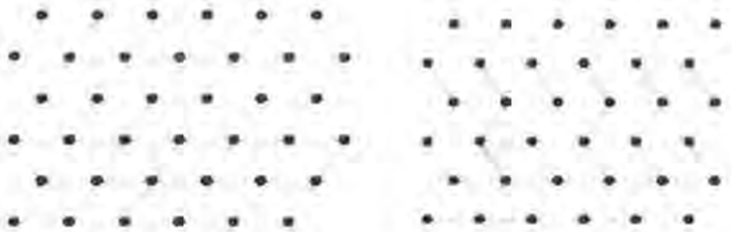

Figure 3. Slipping (left) VS. Twinning (right) (Anadón, 2002).

The actual process of the atoms rearranging during the phase changes could occur in one of two ways for solids. The picture on the left with all the shapes turned the same way is known as slipping (Figure3). On the right is an example of twinning, where the rows alternate which direction the shapes face. In the slipping process, bonds between the atoms have to be broken and remade with different atoms, so this is an irreversible process. In contrast, twinning is a reversible process because none of the bonds are broken, only deformed to make this new shape. Because SMAs can return to their original phases, they have to use the twinning process to transform from one phase to the other (Anadón, 2002).

The last aspect of the shape memory effect involves the ability to "memorize" the set shapes for the individual phases. SMAs can have either one-way shape memory, where they can only remember how to get to the set shape for the austenite phase from the martensite phase. Or they can have two-way shape memory, where the martensite phase also has a set shape and the SMA can remember how to transform into both set shapes during transformation. At first, all SMAs start off with the one-way shape memory ability. This means that they are able to change into the set austenite shape with heat, but whenever the metal cools down to the martensite phase, the SMA will stay in the same shape despite being in a different molecular phase. Because the SMA returns to the martensite phase when it cools, it can be manipulated back into original shape it was in before the transformation by an outside force due to the martensite phase elastic property. However, the SMA will not be able to change back on its own without an outside force.

After numerous repetitions of this movement done by an outside force, the SMA can acquire the two-way shape memory ability, which means it could return to its original set martensite shape with cooling on its own. The key is that SMAs cannot learn this ability on their own, it requires something forcing the cooling SMA back into its original shape in order for the SMA to learn what the martensite set shape is. Also, no SMA innately has this property, it is a learned property over hundreds if not thousands of repetitions that occurs both in the lab and in the field.

The History of SMAs

The first encounter with a novel material similar to shape memory materials was with gold-cadmium (Au-Cd), alloy in the 1930's. Au-Cd has the typical SMA properties, but its transition temperature is above 500°F. So, there were not as many practical uses for it. A little later, in 1938 it was discovered that a copper-zinc (Cu-Zn) alloy, or brass, also had the shape memory effect. While brass was crafted dating back all to 500 BC, it was not harnessed for its shape memory abilities until 1938. But until the 1960's these metal alloys were only an interesting phenomena and they were not necessarily used for anything. Then in the 1960's, the Naval Ordnance Laboratory discovered the SMAs that are still the most common SMAs today, nickel-titanium (Ni-Ti) alloys. Ni-Ti alloys are commonly known as Nitinol, which stands for nickel titanium Naval Ordnance Laboratory. This alloy is approximately 50% nickel and 50% titanium. However, these percentages can be adjusted to change some of the properties of Nitinol such as its superelasticity, transition temperature, or tensile strength. Copper is also added to this binary alloy sometimes to create a tertiary NiTiCu alloy, which is known to change its shape memory properties (Feninat, 2002).

While SMAs were gaining popularity in the engineering world in the 1960's, it took the medical device market until the 1980's to realize their potential and make a new home for

SMAs. Scientists were researching the possibilities of SMAs in medicine in the 1970's, but as is typical of medical research, it was a long and tedious process to ensure the safety and biocompatibility of SMAs. During this time, Andreasen and Morrow published their research on the benefits of NiTi orthodontic wire over the orthodontic wires that were commonly used at that time. Slowly the SMA empire was beginning to build in medicine. In the 1990's the first commercial SMA stent was sold, which has been a mainstay for SMAs in medicine and continues to be improved upon today. Along with this, Britain reported in 1990 that only the use of a self-expanding stent, or one comprised of SMA, could be used for the palliation of oesophageal carcinoma successfully because of the ease of inserting them and the SMAs efficiency. The Simon Nitinol Filter was accepted by the U.S. Food and Administration as a device for treating pulmonary embolisms, or a clot in one of the arteries going to the lungs, in the 1990's as well (Morgan, 2003). In 1998, the TiNi Alloy Company reported that many devices of various sizes and functions had been introduced for medical and that the sales of these devices had reached "more than a hundred million USD per year" (Feninat, 2002). As the market continues to grow and globalization sweeps across the world, SMAs will continue to grow along with them. SMAs have now spread into many fields of medicine including orthopedics, cardiology, interventional radiology, gynecology, and many others (Morgan, 2003).

SMA Applications Outside of Medicine

SMAs are also commonly used in a variety of non-medical applications as well. For example, aerospace engineering uses them due to their reliability and duration during countless cycles of movement. In space, the environmental temperature can drastically change depending on where the object with the SMA is. Therefore, there has to be another way to heat the SMA instead of using heat from the environment as they do in medicine. An electrical current works perfectly to induce the phase change, and is one of the ways heat was induced into the SMAs in the research experiments. SMAs have also been used to make the frames of prescription eye glasses so that if they get bent, they can be quickly bent back into their proper shape with the application of modest heat from the body. Another application of SMA is in motors by using SMAs attached to a wheel and hot water. The phase transformation as the SMA moves in and out of the water is used to rotate the wheel. The kinetic energy can be used for moving an object or to be converted into another energy source to be stored for later (Figure 4). One power plant had been designed with this SMA wheel idea being the center of their renewable energy power source. Unfortunately, this idea did not reach full its maturity with the steep competition of the nonrenewable energy power plants.

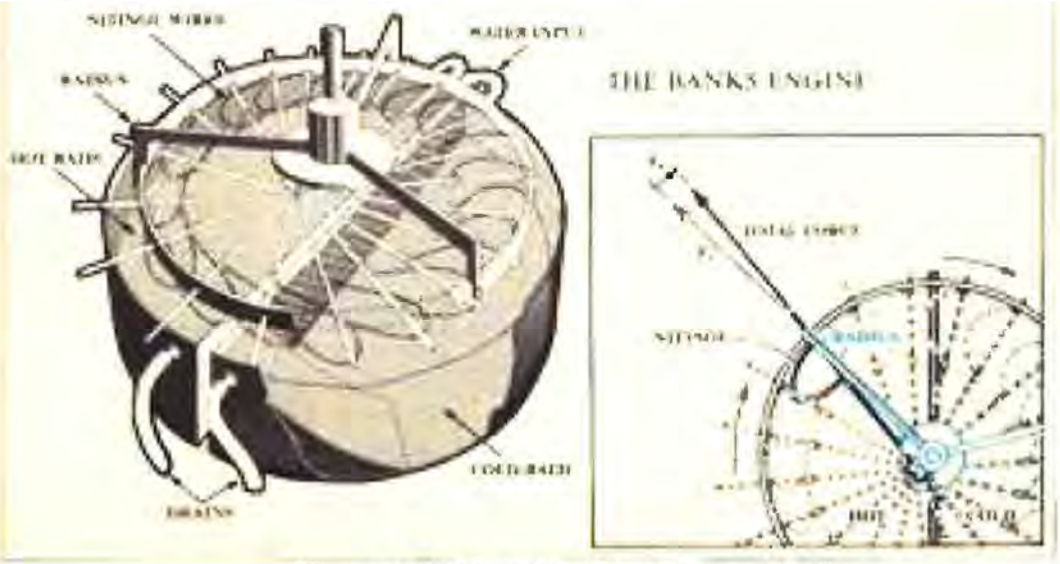

Figure 4. SMA motor (Free Energy, 2015).

Research

In the summer of 2017, research with Dr. Angela Douglass through the J.D. Patterson Summer Research Program at Ouachita Baptist University was done to design and build a solar panel system to be used on campus. This project left an abundance of freedom to imagine what possible outcomes could come from this project. At first, the purpose of the solar panel was to power a street light for a sidewalk on campus. Instead, it was decided that the solar panel could get more use as a charging station for students to do their homework at outside. This way would also attract more people to the project. Next, the idea of a tracking mechanism, making the solar panel track the sun, to increase efficiency of the system was envisioned. During this time is when SMAs were first discovered and their potential was quickly realized for this project. A tracking mechanism using Nitinol, a SMA, was designed that would rely on heat from the sun being condensed through Fresnel lenses to transform the SMAs and turn the solar panel. Bimetallic strips are also commonly used in passive tracking solar panels, but the decision to go with Nitinol was made because of the spring shape and increased travel. Bimetallic strips are similar to SMAs in that they are mixtures of metals that change shape with the application of heat. However, they are generally much thicker, contract shorter distances, and have unfavorable transition temperatures.

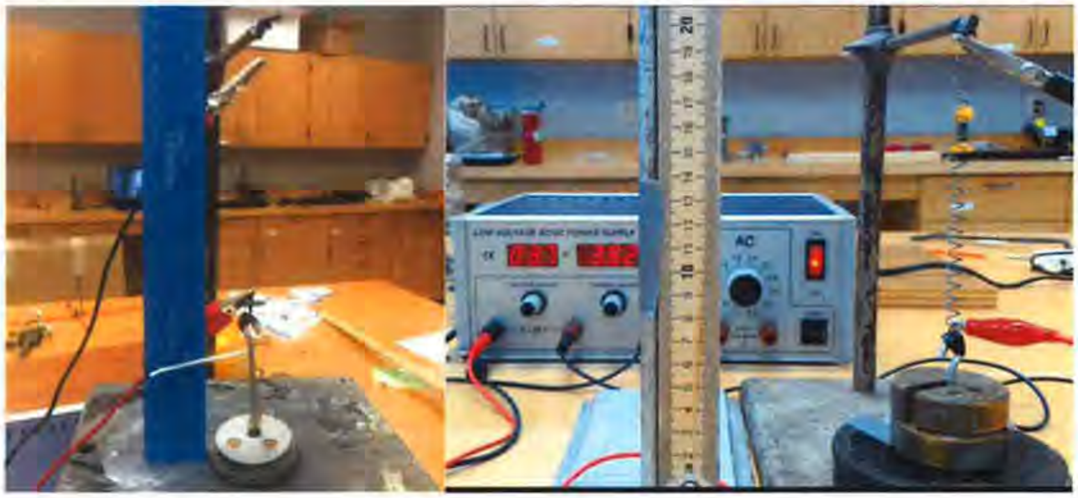

Figure 5. Research experimental set-up. On the left, SMA wire is attached to a ring stand with a known weight attached to the bottom. The clamps are connected to a low voltage power supply (seen in the picture on the right) which is the heat source for this experiment. On the right, an SMA spring is being tested the same way.

Once the design was set up, testing was done on different shapes and thicknesses of Nitinol wire. In these tests, Nitinol was attached to the top of a ring stand and attached to a known weight at the bottom. Then the SMA was heat activated by an electric current to quickly and completely heat the entire SMA, which would be substituted for condensed sunlight in the final product (Figure 5). As the Nitinol changed from the martensite phase to austenite, the contraction was recorded with the camera on a Surface Pro and inserted into the program Tracker to measure the travel distance, time, and velocity of the movement. These experiments showed that SMA diameter was directly proportional to the strength of the contraction and that the spring shape contracted much further than the straight wire (Figure 6 and Table 1).

Table 1. Wire diameter strength.

Wire Diameter (µm)	**Mass (g)**	**Percent Contracted (%)**
125	115	4.28
	223*	4.98
	250	4.02
	300	4.86
250	105	8.00
	800	4.79
	895*	4.28
375	1565.2	3.67
	2065.1*	3.78

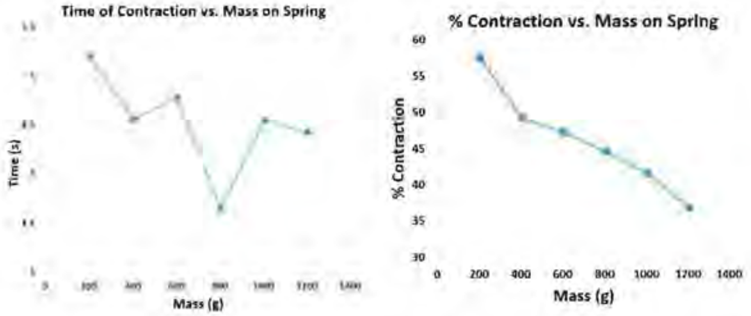

Figure 6. Results from 2017 summer experiments. The graph on the left shows how long it took for the SMA spring to contract with the corresponding weight. The downward slope indicates that more time is needed for contracted against larger forces. The graph on the right shows what percentage of the total length the SMA spring was able to contract with the corresponding suspended waits. Again, there is a downward slope, indicating that the SMA springs cannot contract as far when larger forces are inhibiting contraction. The larger the oppositional force, the longer the contraction will take and the less distance it will contract.

While multiple models were created out of K'nex pieces and PVC pipe, a final passive tracking solar panel has not been finished yet due to time constraints. However, this research helped lay the foundation for the future works of summer researchers to build on. Today, there is a solar powered charging station on campus, however, it is currently stationary and the tracking will be added after further testing can be done.

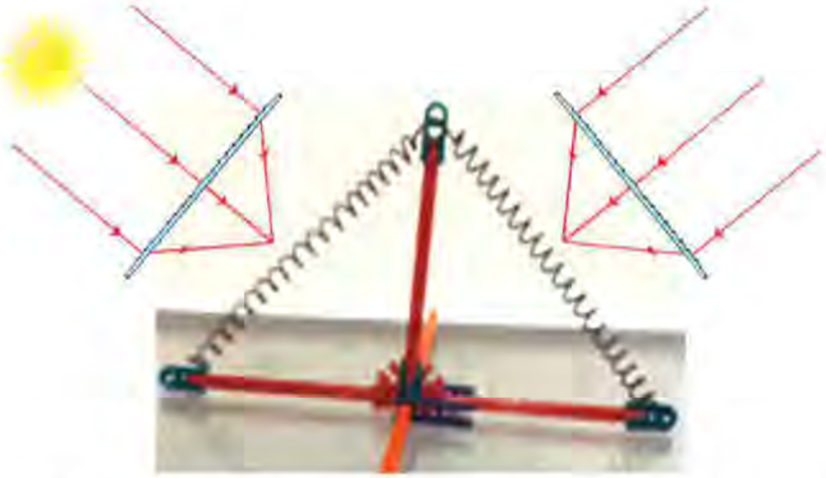

Figure 7. K'nex model of solar panel system rotor. This rotor would be attached above the solar panel with the orange piece being the axis the solar panel lays on and the red pieces and springs perpendicular to the solar panel. The sun is on the left in this picture so the Fresnel lens would focus the light onto the left SMA spring. The light condensed light would heat this left spring, causing it to contract. This contraction would rotate the solar panel with it to where it now faces the sun.

While the SMA application was amazing in this research, there are some drawbacks with SMAs. First of all, they can be much more expensive than a less sophisticated metal, such as stainless steel. When the shape memory ability is not essential, SMA become easily replaced by cheaper metals. In the context of this research, the shape memory ability was needed to provide the movement in the solar panel system. However, a different passive tracking mechanism could have been used. Volatile liquids, like dichloromethane or Freon, provide another option for passive tracking similar to SMAs. One tank containing the volatile liquid would be on each side of the solar panel with mirrors surrounding the backside of the tanks to reflect light back at the volatile liquids. Then as light would shine on one side more than the other, the liquid would evaporate on the side receiving more light and alter the solar panels center of gravity and turn it towards the light till it balanced out. SMAs were chosen over volatile liquids because of the dependability and durability of SMA over volatile liquids. Also, volatile liquids frequently have to refilled and are very toxic if mishandled.

Another option is to actively track the solar panel using power from the solar panel to power a motor that turns the panel. This can be done by using a camera and computer to monitor the sun's location and turn the solar panel accordingly, or by having photoreceptors on the sides of the solar panel to determine where the solar panel needs to turn to even out the amount of light hitting all the photoreceptors. While active tracking can be more accurate than passive tracking, it is also more expensive and less efficient on smaller models because of the consumption of power needed to rotate the solar panel (Mousazadeh, 2009). For the sake of simplicity, cost, efficiency, and dependability, SMAs were the choice for the solar panel system.

SMA Applications in Medicine

There are numerous applications of SMAs in medicine today. So many that it would be impossible to include them all here. The ability to manufacture an alloy with a favorable transition temperature is a big component to why they are used as much as they are, as well as their superelasticity, durability, and biocompatibility. Transition temperatures can be used in a couple of ways. One way is to set the transition temperature close to body temperature. This configuration allows for manipulation of the SMA prior to being exposed to the body's environment, whether that be outside of the body or inside a concealed capsule being inserted into the body. Doctors use this technique for many devices such as stents, orthodontic wires, bone grafts, staples, and catheters.

The SMA stents are an example of an encapsulated SMA (Figure 8). These stents are used to open up the closed blood vessel, restoring adequate blood flow to what was a closed blood vessel. First, the stents are compacted into a sheath that is inserted into the blood vessel of interest upstream from the portion that is blocked off. Since the temperature inside this sheath is below the SMAs transition temperature, the SMA will remain in the superelastic and malleable martensite phase. Next, the SMA-sheath combination is moved along the blood vessel until it reaches the area of interest. Because the SMA is compacted, it can fit inside this narrowed blood vessel. At this time, the SMA is released from the sheath and is exposed to the body's temperature. The SMA then expands as it transitions into its preset shape of the austenite phase, applying pressure against the inside walls of the blood vessel, and causing it to open. The SMA will remain expanded, since the body temperature is nearly constant, and will continue to hold open the blood vessel . In many cases, the blood vessels grow around the SMA stent and the two become one. There are cases of the blockage returning after this kind of treatment, but generally SMA stents are better at preventing this from happening than other courses of treatment (Morgan, 2003).

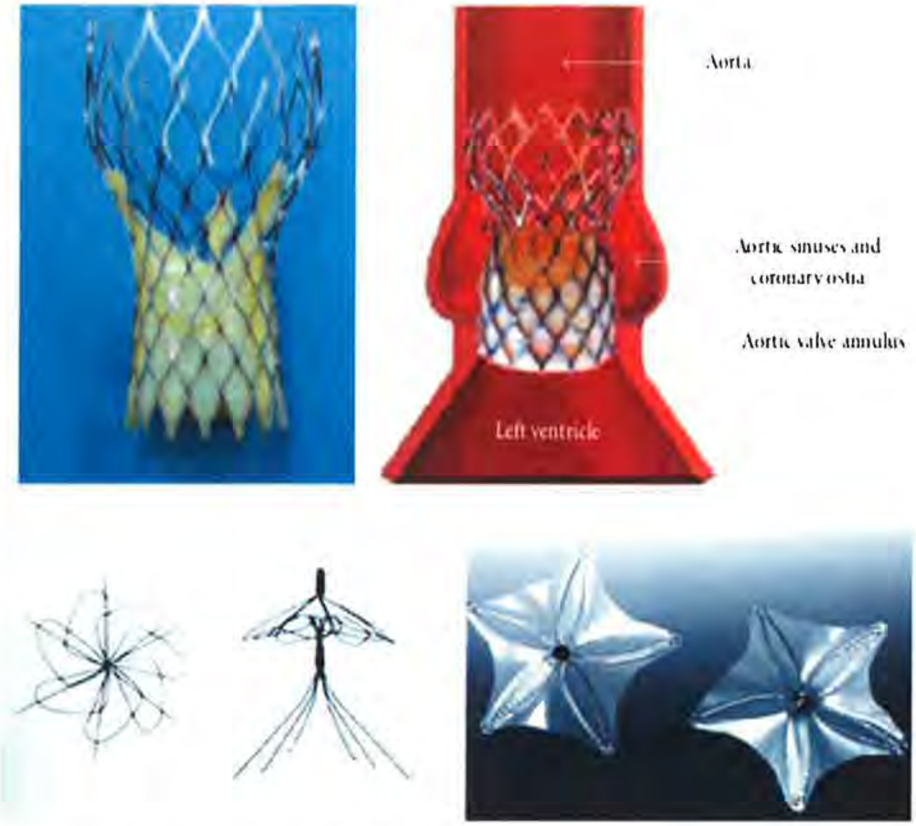

Figure 8. The two pictures on the top are stents trying to open an artery for blood flow (Morgan 2003). Bottom two pictures show a device used to block unwanted blood flow.

SMAs can also be used to close off areas of blood flow that are not meant to be open. The same mechanism is used for closing an unwanted open pathway that is used for opening a pathway. This is the case with ventricular septal defects, or holes in walls that are supposed to separate the two ventricles in the heart. The only difference is that instead of the middle of the SMA being hollow, there is a material in the middle acting as a curtain and blocking the passage of blood. This can be thought of as inserting a closed umbrella into an open window and opening it to create a barrier that seals the entire window, effectively blocking any rain from entering the house from the window (Figure 8).

Another example of SMAs with a transition temperature at body temperature is orthodontic wire. Unlike stents, orthodontic wires are manipulated in the martensite shape outside of the body to an approximate shape of the patient's mouth. Whereas the SMAs in stents are protected from body heat in the sheath, and the wires are immediately exposed to a change in temperature because they are not covered. This temperature change causes an immediate phase transformation, which applies a contractile force on the teeth into the position of the preset austenite shape of the SMA. The SMA wire is attached to anchors that are glued onto each tooth, therefore, applying force to the teeth. Another difference from the stents is that these orthodontic wires can be used to both spread teeth apart or bring teeth closer together. When braces are first applied, a thin SMA wire will be used to apply a small force. Then as treatment continues, thicker and thicker wire will be used to apply more force on the teeth to move them further into the desired shape. The strength of the wire increases proportionally with the wire diameter as the research has shown.

Another major medical application of SMAs are surgical tools, such as guidewires. They differ from orthodontic wire and stents because they are in the austenite phase prior to being used inside the body. This lack of a phase change is due to their lower transition temperatures. The lower transition temperature gives the guide wires more rigidity than they would if they were in the martensite phase, while also providing a little flexibility. The most important characteristic of the SMA in these guidewires is the resistance to kinking because, while other metals might have similar tensile strengths, none of them have the ability to uncoil themselves like SMA alloys do by having the preset austenite shape be in the form of a wire. Therefore, if the wire were to wrap around itself after bumping into numerous obstacles inside the body, the SMA would ultimately straighten itself out after it was freed from whatever was blocking its path.

While SMAs are biocompatible for the most part, they can potentially become toxic. While titanium is safe to the human body, nickel is very toxic. There have been cases of improper coatings causing nickel toxicity in patients with Nitinol devices placed into them, and there is research to back up these findings. Typically, surface modifications such as electropolishing improve the corrosion behavior of NiTi, forming a titanium oxide layer around the SMA that prevents nickel from diffusing into the body. Electropolishing works by increasing the amount of nontoxic titanium on the surface, creating a better titanium oxide layer. These surface treatments sometimes fail due to the cracking of the titanium oxide layer. Cracking can occur during deformation when the shape memory effect is occurring (Feninat, 2002). However, NiTi biocompatibility has held up in numerous *in vitro* studies measuring cellular tolerance and cytotoxicity and Nitinol did not affect cell growth (Petrini, 2018). Today, NiTi alloys are widely recognized and accepted for medical use because they has proven to do no harm in the vast majority of its applications (Feninat, 2002). Morgan states that SMAs "offer advantages over conventional medical procedures that…indicate that Nitinol is certainly biocompatible for specific applications" (Morgan, 2003).

Possible Future Applications

While doing different research at Arkansas Children's Hospital in Little Rock, Arkansas, many shadowing opportunities in clinical situations as well as in the operating rooms (OR) were available to the student researchers. One of these shadowing opportunities in the OR included the Nuss procedure being performed. The Nuss procedure is a fascinating surgery that is both functionally and cosmetically appropriate for correcting severe pectus excavatum, a sunken chest. A sunken chest refers to the sternum, the chest bone in the middle of the chest, lying deeper and more posteriorly, or further towards the back, than normal. While most people can function normally, for some the abnormality is so bad that it impairs the lungs from being able to inflate all of the way. Whether it impairs breathing or not, a sunken chest can be an insecurity for many people, so it is often corrected with the Nuss procedure in many adolescents (Figure 9). In the Nuss procedure, a curved metal bar is inserted underneath the ribs and the sternum that can hold the thoracic cage, the ribs, sternum, and thoracic vertebrae, in the proper shape with the curved bar pointing anteriorly, or towards the front of the patient. In order for this to happen, the bar must first be inserted facing in the opposite direction so that it can bend down underneath the sunken sternum and ribs and extend to the left and right side of the thoracic cage. Then, almost like a medieval torture device, the doctors grab the sides of the bar on each side of the patient and crank it around to turn the bar so that it is now pointing in the right direction. While the current state of the Nuss procedure has proven to work, is there not a better way to perform this operation? One that is not as harsh for what is ultimately a cosmetic surgery for some people?

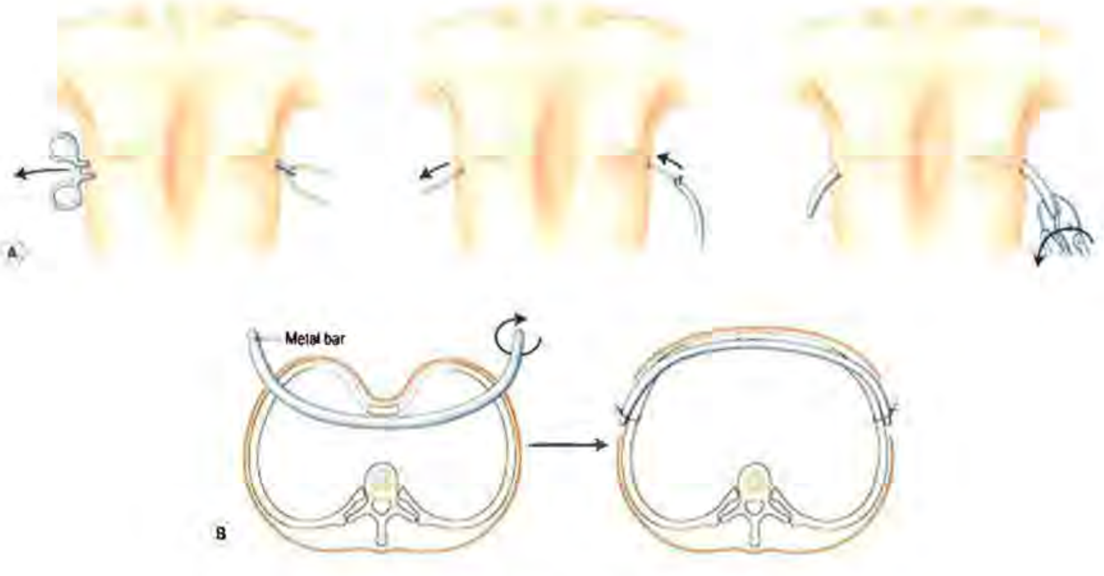

Figure 9. Nuss procedure (Yildirim, 2018).

SMAs could help to lessen the harsh cranking and grinding of bones and metal in this operation by replacing the metal bar with a SMA. By replacing this bar with a SMA that has a transition temperature just below body temperature, the SMA could do the movement from bent underneath the sunken chest to propping the chest up for the doctors. It would work similarly to how the stent works by being concealed in the martensite phase until the proper time. Then being released to the body's temperature and environment, causing it to transform into the austenite phase and it's preset shape. Not only would this be this easier on the doctors, but much easier on the patient's body. Instead of abruptly applying this force and grinding against the sternum, the SMA would transform itself to flex against the sternum, applying a smooth a constant force. With the correct SMA that has enough thickness and strength, this could possibly be done. However, this is only a theory and serious research and testing would need to be done before this could ever become a real possibility.

Conclusion

Since their discovery, SMAs have made a significant impact in the engineering world. They have been used for countless applications from astronomical devices in space that are literally out of this world, to helping orthodontists give people radiant smiles. SMAs will always have a place in SMA researcher's hearts, not literally like those who have had their ventricular septum defects corrected, but figuratively from the research and studying that has been done with them. To think that such an amazing and universally used alloy has not yet become common knowledge like other metals such as stainless steel is surprising. SMAs affect mankind in ways that it is not even aware of, and they still have the potential to do more. Even if one does not care about medicine, engineering, manufacturing, or technology, it would not be wise to turn a blind eye to its impact in the medical device market alone which was "estimated to be more than US$130 billion in 2002" (Morgan, 2003). SMAs made their appearance in the 1960's and continue to make an impact on people's lives today. More research into these awesome alloys needs to be done so that they are used to their maximum efficiency whether that be in new mechanisms, like with the Nuss procedure, or in improving current SMA using technologies.

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