APPLICATION OF SHAPE MEMORY ALLOYS IN MEDICINE

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Shape memory phenomena is strictly related to the reversible martensitic transformation which occurred by cooling over stressing. The overview of some papers on biocompatibility and corrosion behaviour after passivation of NiTi alloys are presented.

The shape memory effect and superelasticity application to medical purposes are described basing on the last published works.

The advantage of the devices using the shape memory and pseudoelastic are stressed when compared to the traditional steel applications in medicine. Staples, stents, simon nitinol filter, Mammalok needle wire and Amplatzer septal occlusion device applications are illustrated and discussed.

Introduction

Shape memory effects in alloys are strictly associated with the martensitic transformation which rely on their structure change (atomic rearrangement) during cooling or heating through their characteristic transformation temperatures or stressed and released into certain limit. This means that the martensitic transformation is reversible and is thermoelastic in nature.

The only shape memory alloys used for medical purposes are nickel - titanium alloys with the near equiatomic NiTi composition.

The unique characteristics of shape memory and superelasticity, acceptable resistance to corrosion and biocompatibility exhibited by nickel - titanium alloys have been exploited in the manufacture of biomedical devices. Shape-memory and superelastic implants have recently aroused wide interest in the medical field and a number of proposed applications have been discussed in review papers [1-4]. One of the latest overview of nickel - titanium alloy medical application summarises the achievements in this field, emphasises their significance for the development of the medical technique and expresses the expectation that the use of these alloys in medicine will increase [5].

Martensitic transformation in NiTi alloys

The martensitic transformation is diffusionless i.e. there is no randomwalk mixing of atoms or atom-by-atom jumping across the interface. Consequently the product phase (martensite) inherits the same composition, atomic order and lattice defects as in the parent phase. The martensitic transformation is displacive, that means that there is a coordinated shift of atoms. Sometimes it is discriptively referred to as a "military" transformation. It is presumed that the atoms move in an organized way relatively to their neighbours but these motions can only be inferred from experimental knowledge of the initial and final positions of lattice sites.

One of the main reason for the reversibility of thermoelastic martensite is that there are inherently low elastic strains associated with the crystal structure change, so that the elastic limit of the parent phase matrix is not exceeded and irreversible plastic deformation does not occur. Futhermore, the strains which do build up as the martensite plates grow are effectivelly cancelled out by forming groups mutually accommodating plates.

The reversible martensitic transformation is realized when martensite forms and grows continuously as the temperature is lowered and shrinks and vanishes continuously as the temperature is raised. This is schematically shown on FIG.1. The martensitic transformation on this scheme is performed as a shear of the parent lattice. [6]

The transformation of B2 type parent phase lattice of NiTi alloy to the monoclinic lattice of martensite marked as B19' is shown on FIG. 2.

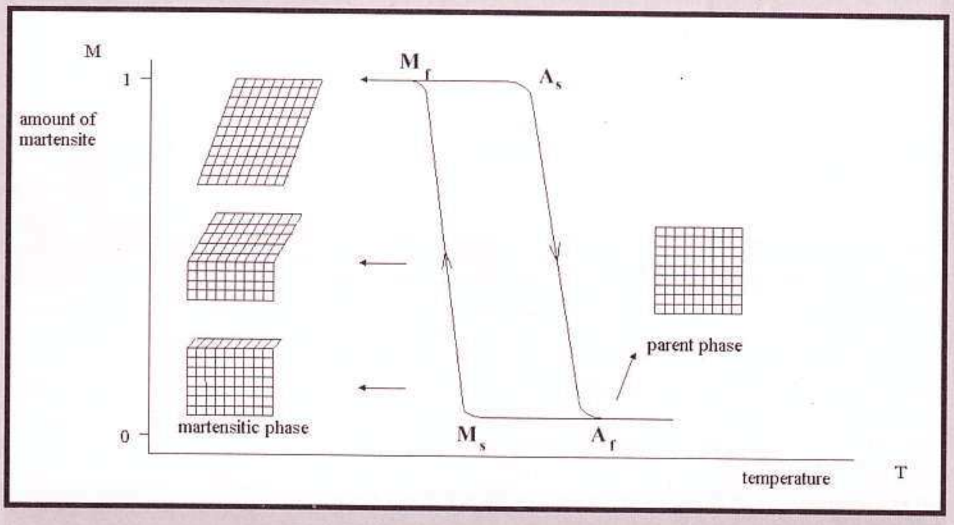


FIG.1. The transformation of parent phase to martensite is shown schematically by shear.

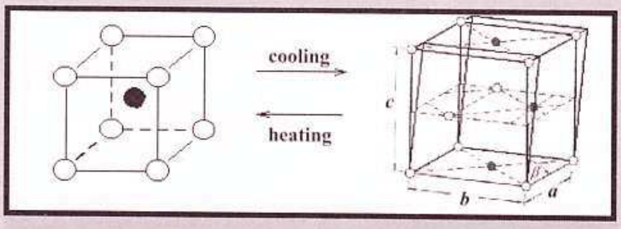


FIG. 2. Lattices of the B2 - parent phase and B19' of the martensite.

Shape memory

As it was mentioned before, the shape memory phenomena are directly associated with the reversible martensitic transformation. [7] Tree different phenomena can be distinguished:

A) one-way shape memory effect

B) two-way shape memory effect
C) pseudoelesticity

A) The one-way shape memory effect is achieved by deforming the martensite at constant temperature and then heating it up to higher temperature. During heating the sample recovers its original shape. Let us consider the one-way shape memory effect on example of FIG.3. The sample at the room temperature is in martensite state and will be deformed up to some limit. Then during heating by achieving the As temperature the martensite and associated strain start to disappear. At Af this process is finished and the material consists of the parent phase. During next cooling the strain does not change, the predeformation shape is stable. Because the shape changed only during heating but not during cooling the phenomenon is called the one-way shape memory effect. Of course during cooling below M_s the parent phase starts transforming to the martensite again, but this martensite is obviously unstrained.

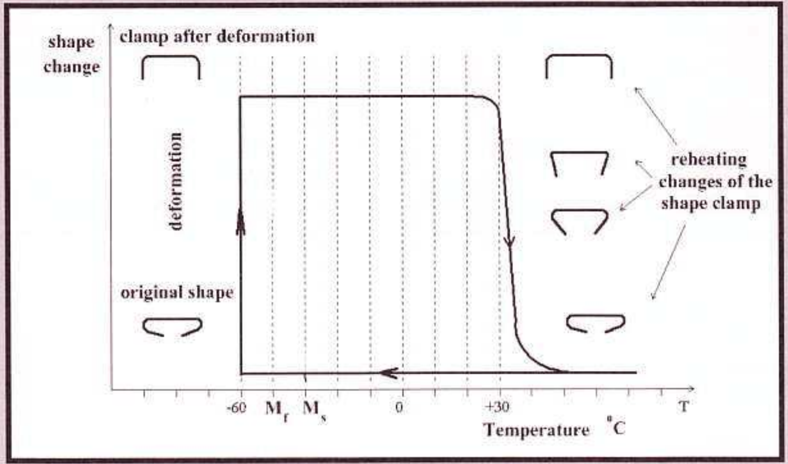


FIG. 3. Illustration of one-way shape memory effect.

On the same figure as an example of illustration this one-way shape memory effect the shape change of a simple surgical clamp can be see. Starting from the original shape, below Mf the arms of the clamp are straighten by deformation, and then during reheating in the range of the revers martensitic transformation A_s-A_f the shape recovery is completed.

B) In the situation when the shape changes during heating and colling this effect is called the two- way shape memory. The change of the shape occurs without any external stress and the material remembers the shape of the parent phase as well as of the martensitic phase.

This two-way shape memory effect can be achieved by a special training procedure to inducing the effect. The essential feature of such a training is the repeating of the martensitic transformation under external stress, this process induces the martensite plates of determined orientation in regard to stress direction.

C) Pseudoelasticity or superelasticity- this effect is connected with the stressing of the parent phase (above A_f temperature) and inducing the martensitic transformation. The transformation proceeds continuously with increasing applied stress and in reversed continuously when the stress is decreased as seen in FIG.4. The section AB represents pure elastic deformation of the parent phase. At point B, corresponding to stress σ^{P-M} the first martensite plate start to form. The transformation is essentially complete when point C on the curve in reached. On continued stressing the material which is completely in martensitic state deforms elastically. At point D the plastic yield point of the martensite is reached and the material deforms plastically until fructure occurs. If the stress is released before reaching point D i.e. at the point C' the strain is recovered. When the stress reaches the σ^{P-M} the reverse martensitic transformation starts and the fraction of martensitic decreases until the parent phase is completely restored. This curve represents the behaviour of a single crystal; in policry-stalline materials the reversible strain is lower. The main feature of the pseudo-elesticity is the unusual high elastic strain which for single crystals may be as high as 20% (for policrystallines about 8%).

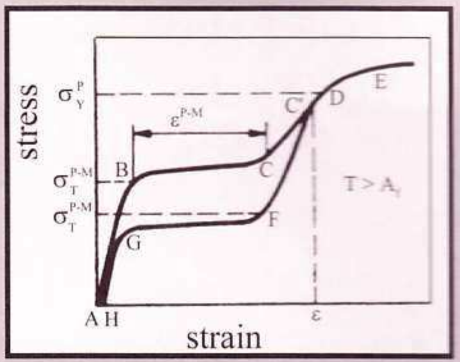


FIG.4. Scheme of superelasticity - martensitic transformation under stress.

Biocompatibility of NiTi

The unique properties of NiTi have provided the enabling technology for many applications in the medical and dental industries. This application encompass from surgical tools to permanent implants, also the implants within the bloodstream.

The excellent biocompatibility, very high corrosion resistance and excellent cytocompability of NiTi has made these applications possible. The nickel and titanium in the NiTi are chemically joined by strong intermetallic bonds, so the risk of reaction, even in patients with nickel-sensitivity is extremely low.

NiTi materials naturally form an oxide layer on their surface during processing into the finished form. The oxide that forms on the surface is primarily TiO_2 and medical products have demonstrated acceptable biocompatibility with the natural oxide on the surface. The oxidation film on the surface may be obtained by thermal oxidation, electropolishing, and chemical passivation as suggested by ASTM F-86.

Chemical composition of this protective film could be either pure oxides or a mixture of oxides and hydro-oxide. The structure of this film could be either a polycrystalline, or an amorphous in nature, or a mixture of polycrystalline and amorphous depending on the process of surface treatment. Thermal oxidation would produce a layer of polycrystalline oxide on the nitinol surface, a high concentration of hydrooxide film could be formed under electropolishing condition.

ASTM recommends passivation of implant metallic material prior to implant in order to have a proper corrosion resistance to the body fluit. This passivation process would create a layer of some kind of oxide on the metallic implant surface. Amorphous oxide is indicative of adequate and proper passivation. The absence of crystalline defects in amorphous oxide like grain baundaries, and dislocations is believed to preclude electrochemical break down.

Amorphous oxide coating on metallic material has been demonstrated to possess the best corrosion resistance under in vitro testing as shown on FIG.5. [8].

Results of cyclic polarization measurements indicate that nitinol devices with a polycrystalline oxide exhibit low breakdown potentials (E_b) and as judged from the cyclic polarization measurement, and show unstable $E_{\propto}$ during long-term exposure to body fluid substitute. In contrast, amorphous ox-

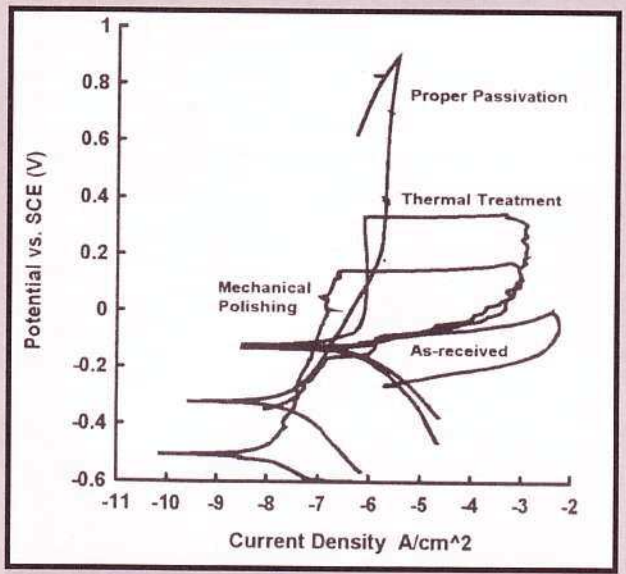


FIG.5. Results of cyclic polarisation measurement for NiTi with different surface treatments. [8]

ide coated nitinol coupon shows the absence of breakdown potential and has steady $E_{\propto}$. The amount of potential difference (Δ_p) between the breakdown potential (E_b) and the open-circuit potential $(E_{\propto})$ plays an important role in the determination of the tendency of pitting degradation. Dp is small for the polycrystalline oxide and is an infinite number for an amorphous coated nitinol sample. No pitting degradation was found after a cyclic polarization test for an amorphous coated nitinol specimen.

Amorphous oxide coating on the nitinol devices would appear to be promising in the corrosion resistance in vitro in body fluid substitute. Any device intended for use as permanent implanting in critical human organs would benefit from being bio-inert.

Corrosion resistance of metallic implants has been usually evaluated in simulated physiological solutions without containing organic substances, for this reason the corrosion behaviour of Ni-Ti shape memory alloy was examined in a cell culture medium containing fetal bovine serum as well as in 0.9% NaCl solution by an anodic potentiodynamic polarization measurement and a polarization resistance method. The absorbed proteins on the alloy surface after immersion in the cell culture medium was analyzed by X-ray photoelectron spectroscopy (XPS). The results shows the strongly influence of the protein molecules in serum on the passivity of NiTi alloy. The presence of serum protains lowered the breakdown potential Eb and increase the passive current density ip. The corrosion rate of the freely immessed condition in the presence of the serum proteins was twice as high as that in 0.9% NaCl solution. The XPS analysis revealed that protein molecules in the serum are quickly adsorbed on the TiO_2 surface film. The protein absorption and a succesive metal - protein complex formation might affect the depassivation process and increase the corrosion rate of NiTi alloy [9].

On the other hand nitinol has shown a good in vitro biocompatibility with human osteoblast and fibroblasts. Despite the higher initial nickel dissolution, NiTi alloy induced no toxic effects, decrease in cell proliferation or inhibition on the growth of cells in contact with the metal surface [10].

The invitro cytocompatibility level of NiTi and vitallium are similar. However these two alloys seem relatively more toxic than such orthopaedic biomaterials like pure grade 1, 4 and 5 Ti and 316 - L stainless steel. Fortunately PTFE deposition increases the NiTi cytocompatibility [11].

Medical applications of shape memory effect

One of the simplest medical application of shape memory are clamps and staples for osteosynthesis which are used for the same perpusos where Blount's bone staples made of conventional implant materials are used. The memory clamps when compared to the Blount clamps have the advantage of allowing the osteotomy gap to be closed tighter after the device has been implanted. The aim of the osteosynthesis should always be to achieve the firmest possible apposition between the two ends of the bone in order to accomplish rapid and reliable healing. This conditions can be fulfilled much better using the memory clamps because the arms are bending to the inside during reheating eliminating the gap and inducing some pressure on both end of the brocken bone shortening the healing time [7,12]. The working principle of the memory staple is shown on FIG.6.

A particular example of shape memory staples application may be mandible bone fracture fixation [13]. The staples were produced of a Ni-Ti-Co alloy that recover their original shape at the temperature of the patiens body. The shape-memory staple is set into the holes drilled in both fragments of the mandible. In a time of less than 2 minutes, under the influence of body temperature, the staple returns to its predetermined shape, with the bend working arms joining the bone fragments.

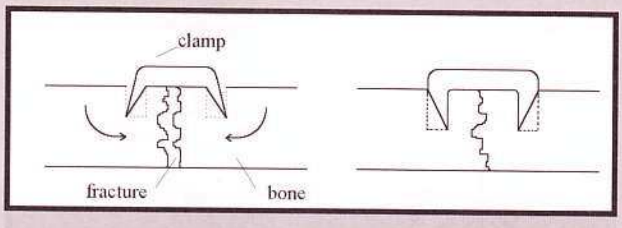
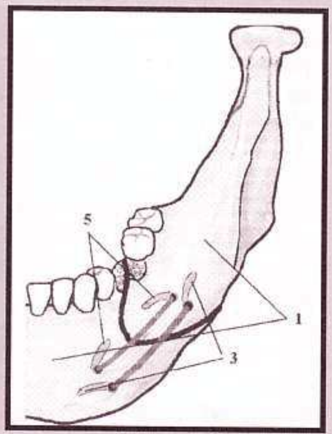


FIG.6. Memory staple before and after reheating.

In cases where the fracture line was diagonal, and the bone fragments were overlapping, two oppositeacting clamps were inserted (FIG.7). After setting the bone fragments in the anatomically corrected position, a clamp with the working arms bent to the outside was first inserted to counteract the compression of these fragments, and then, to achieve better stabilisation, a second clamp with working arms bent inwards was placed. The working arms of the two clamps buried in the bones in different directions also prevented twisting of the bone fragments.

FIG.7. Two staples with opposite direction working arms in a case of oblique jaw fracture
1-fragments of the bone,
3 - staple for stabilisation and prevention of twisting the bone fragments,
5-staple for compression the bone fragments.



Shape-memory clamps are smaller than other implants used for this purpose, and can be placed by an intraoral approach, thus facilitating and shortening the operation. Fractures of all types, both single and multiple, located between the mandibular angels, can be fixed in this way. The clamps ensure complete immobilisation of the bone fragments, making maxillomandibular fixation unnecessary and giving increased postoperative comfort.

One of the well known medical application of shape memory wire is a filter device (FIG.8). During surgical procedures emboli can be dislodged and flow towards the heart, which can potentially block blood flow and cause serious problems. Nitinol filters, such as the Simon Nitinol filter, are placed in the vena cava to trap and break up the emboli.

The filter is collapsed to fit into a small insertion tube, or catheter below its Ms temperature by flowing cold soline solution while inserting it into the vein of a patient. When released of the catheter into the Vena Cava, the large vein from the lower body to the heart, the filter warms to the body temperature and freely recovers it remembered shape to anchor itself in the blood vessel were it can catch blood clots before they can reach the heart and lungs to cause a pulmonary embolism.

Recently a particular interest in medicine is devoted to stents which are small - diameter, thin - walled mesh tubes that are deployed into a vessel or other anatomic duct to provide an internal scaffold that helps maintain an open lumen.

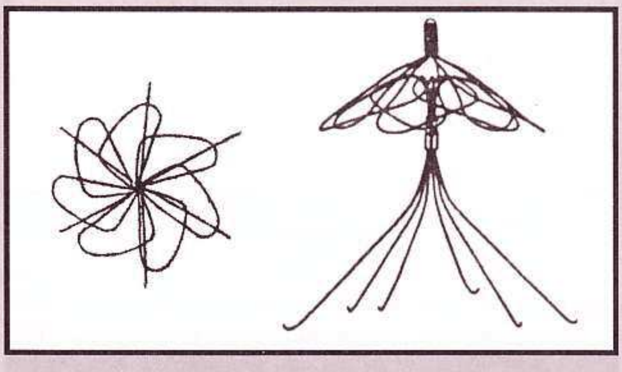


FIG. 8. Simon Vena Cava filter [5].

Stents have demonstrated efficacy throughout the human body, including airway, alimentary tract, urinary tract, biliary tree, and most prominently, the vasculature. Stents are meant to be permanent implants in the body rather than just tools that perform their function and are then removed. They are typically collapsed and loaded into the delivery catheter, sometimes aided by cooling to their martensitic state so they can be easily deformed for loading, and then introduced into the body with the catheter via a natural body opening or through a venous puncture. Once they are located at the chosen site, they are either pushed out of the catheter or a restraining sheath portion of the catheter is pulled back. The stent will then expand in diameter toward its original heat treated dimensions.

The first stents made were just helical coils of wire or ribbon which could be inserted through a catheter after straightening and which would then coil into a tubular shape as they were pushed out of the catheter. These were unsatisfactory, though, due to the rotation as they deployed and also they were not very supportive in the vessel. Later version have been made of twisted or welded wire mesh, knitted or braided wire, rolled up sheet, or folded sheet forms. Currently, the most popular forms of stents are made by laser cutting a pattern into a thin walled superelastic seamless tube, expanding the stent to create an open mesh framework, heat treating this form into the finished stent form and size, then polishing the finished device [14].
A number of stent forms are shown in FIG. 9.

Self-expanding Nitinol stents also have Af temperatures slightly above room temperature, and therefore are technically shape memory devices. One advantage of this process is that it allows the stents to be loaded into their delivery systems and deployed with lower (martensitic) forces. However, once the stents are in place, they react to stresses and strains (e.g., pulsating blood, external forces) superelastically.

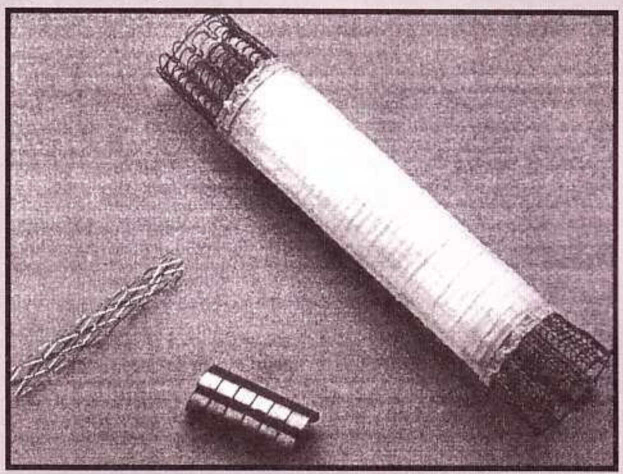


FIG.9. Stents manufactured with Nickel Titanium alloys. [14]

Examples of stents approved by the FDA or in clinical trials include the Cordis S.M.A.R.T. for biliary indications, the SciMED Radius for coronary applications, and the Medtronic AneuRx stent graft for abdominal aortic aneurysms (AAA).

Medical applications of superelasticity

Many medical devices and products from NiTi using the superelasticity phenomena because they can be intentionally deformed into an intermediate shape and then will return to its original shape to undertake the desired shape and function.

One of the typical example of such device is a Homer Mammalok wire shown on FIG.10 mark the location of breast tumour. This is a piece of straight superelastic nitinol wire with a J - shaped bend at one end. It is inserted through a needle to the location of a suspected breast tumor as located by the radiologist, and then pushed out of the needle so the J - book wraps around the tumor. Left behind by the radiologist, the wire marks the location for the surgeon to remove the suspect tissue [15].

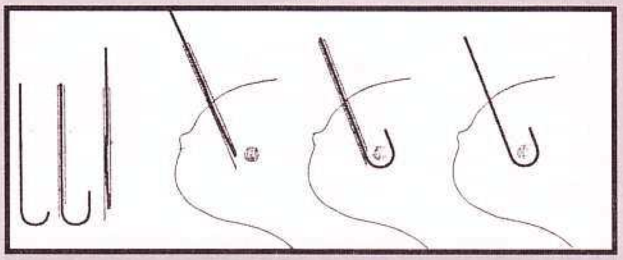


FIG. 10. Mammalok needle wire localizer. [15]

The enormous elasticity of Nitinol allows such alloy devices to be introduced into the body through catheters or other delivery systems with a small profile. Once inside the body, the devices can be released from their constraints and unfolded or expanded to a much larger size.

The most unusual feature of Nitinol alloys is the force or load hysteresis. While in most engineering materials load (or stress, if normalized) increases with deflection (strain) upon loading and decreases along the same path upon deforming strain is finally recovered in a linear fashion. The unloading stress can be as low as 25% of the loading stress.

The "biased stiffness" of a stent made from superelastic Nitinol is illustrated in FIG.11. A stent is compressed into the delivery system following the loading curve to point A. Upon release from the delivery system inside the vessel it expands, following the unloading path of the stress/strain curve. At point B, it reaches the diameter of the vessel lumen, positioning itself against the vessel wall with a low outward force (chronic outward force; COF). As can be seen from the FIG.11 this force remains nearly constant, even if the vessel diameter is changing [16].

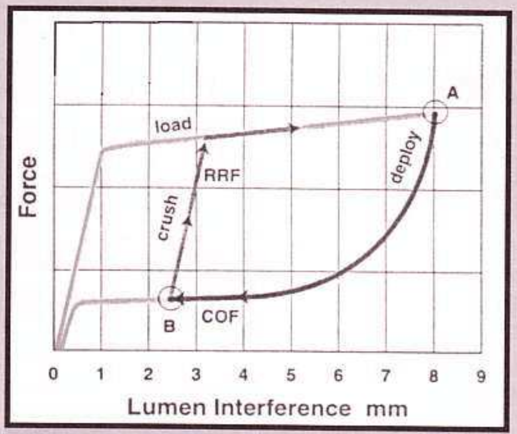


FIG. 11. Deformation characteristics of Nitinol. [16]

A large family of medical devices have been developed which rely on being temporarily deformed, often during their introduction into the body, and then springing into their "remembered" shape to perform their function. Most of these devices are put into the body through a cannulae or catheter, or as a portion of a catheter. Examples include loops, snares, small retractors and baskets or other shapes to catch and hold stones. A recent development is the Amplatzer Septal Occluder device. The device is a Nitinol wire mesh shaped into a "double mushroom" configuration (FIG.12) it can be delivered through a 6 - 9 F catheters.

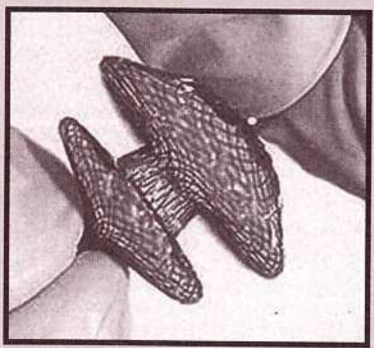


FIG.12. Amplatzer septal occlusion device (AGA Medical Corporation). [16]

Other Nitinol occlusion devices are the ASDOS the AngelWings (MicroVena) and the CardioSeal (Nitinol Medical Technologies). These devices use an umbrella type design, while the PFM Duct-Occlude device uses a Nitinol double helix configuration.

The superelastic wires of Ni-Ti alloys which are able to store the elastic energy found also a broad application in orthodontics to achieve tooth movement through bone remodelling process. The elastic modulus of the NiTi is several times lower than that of the traditionally steels wire what results in lowering the interacting force and increase comfort of this treatment.

Another broad field of application superelastic nitinol are the medical instruments particularly in the minimally invasive therapy.

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