Issues in the Further Development of Nitinol Properties And Processing for Medical Device Applications

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Abstract

Binary Nickel-Titanium is currently a material of choice for many medical devices but there are challenges in fabricating the alloy to the required shape and surface finish. In addition, the properties of the binary are in need of improvement, particularly in the area of radiopacity, superelastic performance and fatigue strength. Alloy developments as well as new approaches to improve properties and fabrication techniques will be discussed as they relate to a variety of devices. The emerging field of MEMS will be reviewed with thoughts on future applications in implantable drug delivery systems.

Background

As the range of medical devices employing Nitinol expands, the demands also increase for better material properties, ingot-melting technology, improved forming methods, superior finish and fabrication techniques. The four decades of working with Nitinol industrial and medical applications has naturally seen great improvements in all of these aspects of manufacturing. However, as implantable devices proliferate with shrinking physical dimensions, so too do demands for further improvements in radiopacity, strength, fatigue and biocompatibility of this alloy family. Since the melting and casting of an ingot is the starting point for the rod, wire, strip and tube used to fabricate medical devices, this is the first topic which should be addressed.

Ingot Melting

The melting of NiTi alloys and the casting of ingots for primary metal working has associated with its challenges of the following nature:

1. Sensitivity to Oxygen and Carbon contamination
2. Requirements for very tight compositional control
3. Solidification conditions to minimize micro and macro segregation
4. Avoidance of non-metallic inclusions

Many of the melting procedures which have been successfully used for titanium alloy production are valid for NiTi. Currently, the most common procedure for NiTi shape memory alloys is to use vacuum induction melting (VIM) for the primary alloy preparation followed by vacuum arc melting (VAR) to improve homogeneity in microstructure. The segregation characteristics are a function of the nature of the phase diagram and the solidification rate; faster cooling rates favor smaller dendrite arm spacing which equates to minimum segregation. Fast cooling rates are also helpful in promoting a good dispersion of particulates such as carbides and intermetallic compounds. Since the VIM process uses graphite crucibles, there is possible pick-up of carbon, however, by avoiding direct contact between titanium and the graphite crucible and by holding the melting temperature below 1450°C, the carbon level can be held to 200 to 500 ppm (1). The general requirements on Nitinol chemistry and trace elements are defined in ASTM standard, F2063-00 (2). The transformation temperature in a relatively small VIM ingot can generally be held to +/-5°C. Controlling micro and macro segregation becomes more difficult with increasing ingot size. To refine the microstructure, the vacuum arc melting process, VAR, is used where a consumable electrode of the VIM melted alloy is melted in a copper mold resulting in a much more homogeneous ingot with far less segregation. Noting that for alloys with greater than 55.0wt % nickel, a one percent deviation in nickel or titanium content will result in a transformation temperature change of about 100°C, analytical techniques do not have the accuracy to predict the transformation temperature. In fact, transformation temperatures and chemistry are more effectively controlled by careful measuring of the VIM metal charge, as illustrated in Figure 1 where transformation temperature is plotted versus charge chemistry and analytical result of the ingots. Although it is possible to make in-situ alloy corrections during the VIM

melting by analyzing samples taken from the melt, this is a difficult procedure in manufacturing [3].

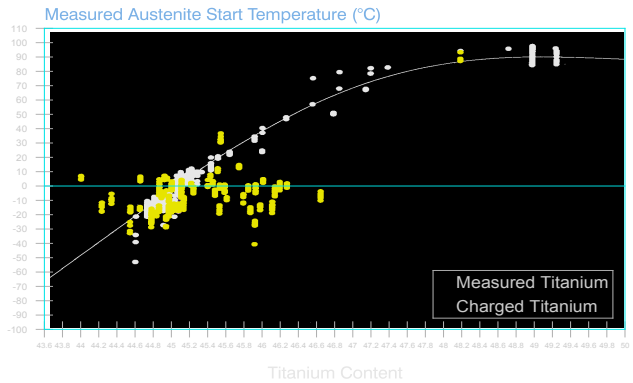

Figure 1: A plot of measured austenite start (As) temperature versus charged (o) and measured (•) titanium contents (Courtesy of Special Metals Corporation).

Alternatively, multiple VAR melting practice is used for commercial NiTi ingot production. Avoiding contact with the graphite crucible, the VAR ingot tends to produce a cleaner alloy with carbon contamination typically less than 200 ppm. Unfortunately the fact that only a small molten zone is produced as the arc progressively melts the electrode, there is a less homogeneous distribution in chemistry along the ingot and the top to bottom ingot transformation may vary greater than 10°C. By repeating the VAR process, so called multiple melting, a more homogeneous ingot may result.

Although the present preferred melting system is the VIM-VAR described, the vacuum induction skull melting process has the potential for producing an ingot of higher purity. In this process the crucible has a very unique geometry, crown like in appearance it has a water cooled base with side stakes consisting of rectangular water cooled rods, spaced at about one-half of the rod diameter. The crucible is surrounded by an induction coil, and the entire assembly is capable of being tilted to pour into molds placed within the vacuum chamber. When the alloy is melted a thin layer of solidified metal is created over the crucible bottom and the stake sides, resulting in the melt being confined in a crucible or skull of the alloy being melted, eliminating the potential for crucible-melt interaction, a minimum of contamination and very vigorous melt stirring. The shell formed over the side stakes shrinks away from direct contact, thus preventing electrical short-circuiting of the electromagnetic field. Since the electromagnetic induction is absorbed by the metal crucible as well as the melt, the process is inefficient and requires a large power source. The maximum sized ingots currently produced are about 40K.

The benefits of high purity Nitinol are yet to be proven. There is evidence that fatigue cracks often nucleate at subsurface inclusions [4], however, the difference in Carbon contents between VIM-VAR and multiple VAR processes does not result in a measurable difference in fatigue resistance [5].

Nitinol compositions with transformation temperatures less sensitivity to compositional variation such as the NiTiCu and the NiTiNb ternaries are available. However, Cu addition leads to hot shortness, a problem in hot conversion while Nb enlarges transformation hysteresis. Other alloying possibilities that reduce compositional sensitivity and improve superelastic properties may exist which would make the ingot process more efficient.

Primary and Secondary Alloy Fabrication

With the exception of investment cast implantable devices such as orthopedic systems, most medical devices are fabricated from wire, strip or tube. As such, the primary processing of the ingot involves a hot break down by either hot forging or rolling. The hot working breaks down the cast structure and provides an acceptable size for further cold drawing. Hot working must be carried out at a temperature which avoids severe oxidation. For Nitinol the preferred hot working temperature is 800°C, a temperature which ensures good workability and minimizes oxide buildup. Hot rolling employing a mill with grooved rolls is the most commonly used break down process. Extrusion has been explored using the Segournet process which employs a molten glass lubricant [6], however this has not been used in current commercial practice.

Once a rod of suitable dimension has been achieved, Nitinol is cold worked to yield a final dimension and, by combining the cold working with heat treatment, achieve the desired mechanical and physical properties. Nitinol has a very high work hardening coefficient, which limits the cold reduction achievable in a single pass. Interpass annealing is carried out at 600 to 800°C, and in most cases the oxide formed is not removed until the final pass since its presence assist in retaining the die lubricant. Lubricants which are commonly used include graphite containing water, molybdenum disulfide, oil based lubricants and sodium stearate soap. Lubricant must be scrupulously removed after the final dimension has been achieved. Round wire is produced in single or multiple die stands, and rectangular wire is produced using a Turk's head bull block process. Round wires can be flattened to yield ribbon, although tolerances are better in the Turk's head drawing process. Nitinol tube has become the major starting point for the production of stents, and, as such, there are several variations on tube drawing processes: floating mandrel, non-deformable mandrel and deformable mandrel. The details of tube drawing methods are proprietary, however several are described in patents. Tubes with an O.D. as small as 0.25mm are being produced. The problems which are being addressed include tube concentricity, tube outer surface finish and tube I.D. cleaning [7]. As in wire drawing, interpass annealing is required, and surface oxidation is minimized by annealing in an inert atmosphere. Cleaning is

particularly important when the tube is to be laser cut since impurities can be incorporated into the recast structure and promote micro cracking before the recast structure is removed.

The use of sheet Nitinol is not as important as the other forms, although an attractive fabrication process is the use of photoetching of sheet. This process is capable of very economically creating complicated shapes, and may become a more important fabrication method in the future. Although sheet can be rolled to 0.025mm in relatively narrow width, for wider sheet, a thickness of 0.25mm and 125 mm width is more practical.

Machining

Machining of Nitinol is very difficult by reason of the very rapid work hardening of this alloy. Although with proper carbide tooling and control of tool geometry, speed and feed, excellent tolerance and finish can be achieved in turning operations. Milling with its interrupted cut is more difficult with tool brakeage a frequent problem. Drilling, as with turning, requires careful control of feed and speed, and the use of chlorinated lubricant is recommended. Taping is extremely difficult and is not recommended. Cylindrical centerless grinding is a useful process for developing a good surface on tubing and wire, and is used for creating a tapered end on catheter guide wires. Other abrasive methods such as abrasive wheel cut off and abrasive water jet cutting are also used in processing Nitinol. Electro-discharge (EDM) machining is quite useful, although not really suitable for volume production. Since a recast layer is developed by the high energy spark, this contaminated layer containing electrode copper and oxides is usually removed. As we mentioned earlier, photoetching is used in special cases for forming stents, filters and baskets. Once the tooling has been prepared, consisting of a photographic image, or multiple images, the process is capable of efficient parts fabrication. Tolerance in the process is 10% of the metal thickness, thus for a 0.025 mm sheet, the tolerance would be +/- 0.0025mm, quite adequate for most components. Three-dimensional structures such as stents can be fabricated by the photoetching process using novel imaging techniques. For examples, using contact film and an elliptical mirror or an optical scanning system in synchronization with numerical controlled part rotation and motion, a desired pattern can be imprinted on the photo-resistance coating on a cylindrical structure before etching [8].

Laser cutting and machining has become a preferred method for creating stents from Nitinol tube. Very complicated geometries are produced using CNC controlled part motion and finely focused pulsed Nd:YAG laser beams. Since this is in effect a melting process, a recast layer is produced on the cut surface. To prevent contamination from surface detritus, the part must be very clean before laser cutting is initiated. The recast layer is susceptible to microcracking and must be removed to ensure a good fatigue life for the component [9]. A heat affect zone (HAZ) is also present and must be removed in post cutting operations. The usual techniques for removing the recast materials and HAZ include electro-polishing, abrasive and vapor blast cleaning. Laser cutting is fast and very flexible, and cut geometry is readily changed through reprogramming of the CNC control. Figure 2 shows examples of finished stents fabricated by laser cutting and subsequent finishing.

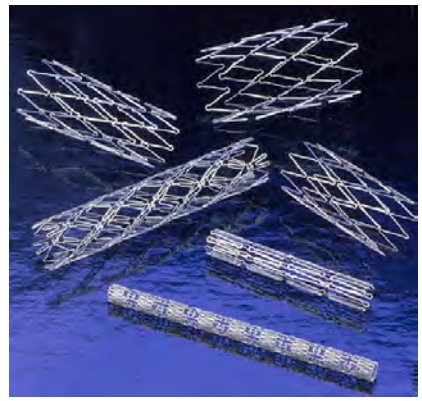

Figure 2: Examples of stents fabricated by laser cutting and electropolishing.

Shaping and Forming

Nitinol materials in either the cold worked or heat-treated state can be easily sheared or stamped (see Figure 3 for examples), but they are difficult to form to an accurate geometry, whether by forming wire shapes or die pressing. The major problem, spring-back, is significant at ambient temperature. To counteract spring back the part can be over deformed so that on release of stress the desired shape is achieved. Unfortunately this leads to the formation of stress-induced martensite which will degrade the desired mechanical properties and shift the transformation temperature. The solution to spring back is to heat treat the part under constraint. Examples of formed parts fabricated by this thermal shape-setting method are show in Figure 4. Where high volume fabrication is required the use of many constraining jigs may be necessary. In another approach to volume production the part can be formed on an insulated mandrel and heated electrically for a few seconds, and then dropped from the mandrel. Only simple shapes can be processed in this manner.

Heat Treating

For the broad range of medical devices which use superelastic Nitinol, the initial condition before heat treatment is 30 to 40% cold work, followed by heat treatment at 500°C. For shape memory alloys, the heat treatment range is preferably 350 to 450°C. Good superelastic performance can also be generated by a solution treatment and aging of alloys with greater than 55.5% nickel. For this treatment, the solution treating temperature is between 600 to 900°C and the aging treatment is carried out at 400°C. This procedure is useful where

forming of a complicated nature can be carried out with the ductile solution treated alloy and then rendered superelasticity by aging. The aging process causes precipitation of the Ni-rich intermetallic compound, and since this depletes the matrix of Ni, the transformation temperature is increased. [10].

Figure 3: Examples of Nitinol stamped parts from strip.

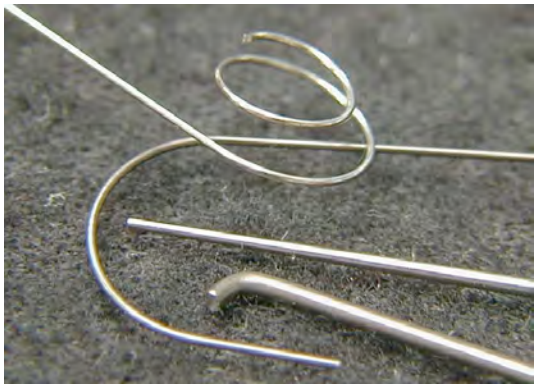

Figure 4: Examples for formed parts of Nitinol fabricated by constraint thermal shape-setting process.

Joining

In the early development of Nitinol actuators and components, joinng was confined to mechanical fastening by crimping, riveting and swaging. Recent development in laser welding processes has made joining of Nitinol to itself a routine process. Contamination by oxygen and nitrogen make it imperative to carry out any joining process involving melting in either a vacuum or under inert gas cover. CO_2 and ND:YAG lasers are both capable of producing welds with excellent strength retention. The CO_2 laser welds do exhibit reduced strength and resistance to permanent deformation in the fusion zone and the HAZ. This is also true of welds made using the tungsten inert gas (TIG) process. Electron beam welding is also useful for welding smaller parts, although the process is slow by reason of the need to load and unload through a vacuum port. The best welds seem to be made using the Nd:YAG laser with a yield of 75% of the base metal strength, and only 0.2% permanent deformation after a 7% strain of a superelastic weld specimen. Resistance welding can also be used, again with adequate inert gas shielding. The Ti rich alloys are more susceptible to weld cracking, although using a consumable wire crack free welds with good strength can be produced.

The adherent oxide surface formed on Nitinol is a barrier to conventional soldering processes. A halogen based flux, as described in U.S. Patent 5,242,759, makes possible soft soldering. An intermediate barrier of nickel, produced by electroplating or electroless nickel deposition creates a surface which will accept solder with mild flux. Another approach is to electroless plate a copper layer using a copper fluoroborate -HF solution, and then follow this with a nickel plating. In some cases a second metal layer, such as gold, over the nickel improves the solderability. Ultrasonic soldering, developed for removing the oxide from aluminum to promote solder wetting, has also been used successfully on Nitinol with a Sn based solder.

There are cases where it is desirable to join Nitinol to other metals, most frequently to a stainless steel. Brittle intermetallic compounds are formed in the fusion zone of such welds, rendering them useless. To avoid the formation of the intermetallics such as FeTi and Fe_2Ti some intermediate layer must be employed which is compatible with both Nitinol and stainless steel. Tantalum is one metal which has the desired characteristics and using this as an interlayer successful welds have been made. Other intermediate layers which can produce similar results are Nb and Mo. Both resistance welding and percussive arc butt welding with a Ta interlayer have yielded acceptable joints.

Finishing and Coating

During hot working of Nitinol the black oxide formed is usually removed prior to cold working using grit blasting, polishing or chemical means. Using aggressive chemicals such as HF there is complete removal of the oxide, but also some removal of metal. Therefore, for fine wires or thin wall tubes care must be taken to avoid significant changes in the desired dimensions of the part. Mechanical polishing, such as vibratory finishing can produce a mirror finish in batch processing. Trial polishing is necessary in order to select the correct medium for the particular part. Electropolishing is a very effective technique for producing a very smooth finish, although consistent results depend heavily on electrolyte and polishing parameters such as voltage and temperature. Mixture of perchloric acid with acetic acid [11] or sulfuric acid in methanol [12] has been used with good results, although the former can be hazardous. .

Corrosion resistance and biocompatibility are both affected by the final method finishing the Nitinol component. The leaching of nickel when the part is in vivo is dependent on the finishing technique [13], with the preferred final surface, being mainly titanium oxide which also enhances the surface passivity, and thus corrosion resistance. Although the smooth appearance of a mechanically polished surface is attractive, in

fact this type of surface has the poorest corrosion resistance while chemical etching enhances passivity [14]. Electropolishing in itself does not necessarily enhance corrosion resistance, however if this is followed with a passivation procedure, an optimum corrosion resistance and biocompatibility can be achieved [15].

Metallic and organic coatings can be applied to Nitinol by a variety of methods. The principal concern in electroplated coatings obtaining good adhesion and ductility to avoid flaking when the part is deformed in service. A damaged metallic coating can also lead to galvanic corrosion. Control of the electroplating process is required to avoid charging hydrogen into the surface which can result in hydrogen embrittlement. Polymer coatings such as Polyurethane and Parylene are routinely applied by dipping, spray coating, co-extrusion and powder coating. PTFE coatings must be cured at relatively high temperatures, circa 300°C, which can have an adverse effect on the mechanical properties.

Powder Metallurgy Processes

Powder metallurgy (PM) is an important route to making precision, high strength ferrous and non-ferrous parts in a very efficient manner. Methods of atomizing have been developed for producing powders of non-reactive and reactive metals, with excellent control of chemistry. When applied to Nitinol the major problem is control of the oxygen content. Typical PM Nitinol parts may have as much as 3000ppm oxygen. Although by careful handling of the powders oxygen levels can be reduced to the region of 1500ppm, there is still concern for the effect on fatigue and ductility.

Atomization of pre-alloyed Nitinol has been carried out using gas atomization, hydriding, pulverizing and mechanical alloying. Blended powders are compacted by hot and cold isostatic pressing, hot and cold uniaxial die compaction and direct powder rolling. A unique process was developed in which powder is loaded into a pyrex glass tube, vibrated for compaction, and then evacuated and sealed. The tube is placed in a vertical furnace where sintering takes place with atmospheric pressure supplying the positive pressure. Given the name CAP [16] for consolidation under atmospheric pressure, it has been successful in producing solid and hollow shapes. The product has 68% porosity and can be further processed by HIP to achieve densities of greater than 95%. Hot working by rolling or swaging can yield fully dense material. By blending in the proper ratio two Nitinol powders with different transformation temperatures one can obtain a sintered product with accurate control of a targeted transformation temperature. The process does not, however, prove to be competitive with VIM/VAR processing.

Elemental Ni and Ti powders can be consolidated by conventional blending, pressing and sintering, but with the mentioned high oxygen content of the product. Since the fusion of Ni and Ti is very exothermic, a container of blended powders can be heated at one end to the ignition temperature which will create a self propagating fusion that moves through the piece. A second consolidation method called thermal explosion is similar, starting with a compacted powder blend, the part is heated to the ignition temperature sintering the part. The products of these processes are very porous and may contain intermetallic phases Ti_2Ni and $TiNi_3$. To achieve acceptable properties, higher density and improved microstructure, these PM derived parts must be hot worked by swaging or rolling. The powder injection molding process has also been tried for the production of small Nitinol parts. Powder is mixed with wax and injection molded into a die, and the part is then dewaxed by heating at a moderate temperature followed by heating to the sintering temperature. Parts which would otherwise be machined can be made by this process. Such parts would not be used where lower fatigue or ductility properties would be a problem.

Porous Nitinol components can be produced by PM processes with porosity ranging from 30-70% with pore size from 60 to 100 microns. Articles of porous Nitinol have been studied for their application in various orthopedic procedures. As in other PM products, porous Nitinol is not ductile, which restricts its application. This topic is discussed in detail in the following paper and in sessions 8A and 8B.

Thin Film Fabrications

Micro electromechanical systems (MEMS) have received a great deal of attention for control of fluidic devices and for applications in robotic systems. Interest in the application of thin film Nitinol MEMS to medical device fabrication has also seen rapid growth. Films can be deposited on metallic, silicon, glass and polymer substrates. Where deposited on cool conductive substrates the deposit is amorphous and to develop shape memory properties the film must be heated to cause crystallization. Although a variety of substrates are used silicon is the preferred material since it can be fabricated by photolithographic techniques [17]. A variety of Ni-Ti alloys have been studied as thin film deposits; the two most frequently employed for MEMS devices are binary NiTi and NiTiCu. Pre-alloyed targets as well as elemental targets are used, although the former produces more uniform compositions. Several types of miniature valves have been developed using the thin film to open and close an orifice in the silicon substrate. A miniature pump system capable of high frequency and high pressure has been produced using a unique deposition technique to produce a thin film with a composition gradient which varies from equiatomic NiTi to a Ni rich composition. The Ni-rich layer of the film acts as a bias to provide two-way memory actuation. When heated the film rises to form a dome and when cool the film returns to a flat position; thus heating and cooling provides a pumping action [18]. MEMS pumps and valves can form the basis for a variety of drug delivery systems and devices of this type will certainly achieve use in the future.

Physical vapor deposition as well as sputter deposition processes are also used to fabricate stents with controlled heterogeneities in properties such as material chemistry, grain structures and surface topography to enhance endothelialization [19]. These deposition processes allow one to manipulate the stent microstructure at the atomic level at the contact surface with blood flow and to create a stent with more predictable oxidation and organic absorption pattern.

Radiopacity

The deployment of stents is aided by observing the position of the stent by radiograph, however, binary Nitinol has relatively poor radiopacity and as a result its image is difficult to see. Stents with coatings of higher atomic number materials such as gold improve radiopacity and provide a clearer image. An alternative has been disclosed in which Nitinol with ternary additions of elements such as platinum, palladium or other elements with high atomic number is rendered more radiopaque. These ternary alloys still retain the desired superelastic characteristics of the binary Nitinol..(20)

Conclusions

Future studies on Nitinol processing will lead to improvements in mechanical properties while maintaining the excellent biocompatibility inherent in these alloys. Topics which important in reaching the goals of alloy improvement are:

- Studies on the properties of Nitinol with very low interstitials: O, C and N.
- Developing efficient, cost competitive vacuum induction skull melting
- Compositions which reduce the sensitivity of transformation temperatures to composition without a negative effect on mechanical properties or biocompatibility.
- A newer approach to alloy improvement using first principals calculations which have already lead to nanoparticle dispersions which improve plateau stresses and UTS.
- Studies of surface coating systems which improve drug eluting performance.
- Thin films deposition techniques to create various stents and medical devices
- Improved numerical modeling at microscopic scale as an improvement over conventional FEA techniques using continuum mechanics.

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