

Fabrication of Nitinol Materials and Components

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Abstract. As Nitinol emerges to find more and more applications in medical devices and industrial commercial markets, understanding on the effects of material processing becomes increasingly important. More so than other materials, properties of Nitinol are significantly affected by its fabrication processes. There are abundant amounts of processing data available in the industry. However, they are often kept proprietary and not released in the public domain. This paper reviews available publications on Nitinol fabrication processes, such as melting, forming, shaping, treating, cutting, joining and finishing, etc., commonly employed or developed for the manufacture of Nitinol material and components. Effects of these operations on the material properties are discussed.

Introduction

Nitinol is well known for its thermomechanical properties of superelasticity and shape memory effect. Along with excellent kink resistance, biocompatibility and MRI compatibility, the alloy has emerged as a unique biomaterial finding an increasing number of medical applications such as orthodontic wires, orthopedic devices, guide wires, stents, filters and components in minimally invasive surgical devices [1]. Development and growth of Nitinol applications in the industrial and commercial markets have also been fairly strong in recent years. Eyeglass frames, cellular phone antenna, high pressure sealing plug for diesel fuel injectors, over-temperature protection device for lithium ion battery are among the applications experiencing significant growth [2].

As more Nitinol products are being developed and produced in mass scale, controlling manufacturing processes to deliver consistent quality becomes increasingly important. Nitinol properties are extremely sensitive to the initial chemistry as well as the subsequent processing. The alloy's flexibility, significant work-hardening rate and high titanium content also pose additional challenges in metal fabrication. Understanding various manufacturing processes and their effects on product performance is the key to successful process controls.

Although significant efforts have been devoted to the understanding of Nitinol processing issues, large amount of the information has been kept proprietary. Present paper reviews available public information related to melting, fabrication, secondary processing methods and finishing techniques commonly used for the manufacture of Nitinol products. The review also includes novel processing methods currently in development.

Melting

General requirements on Nitinol chemistry and trace elements are defined in an ASTM standard, F2063-00 [3]. The Nitinol transformation temperatures are extremely sensitive to a small variation in the Ni or Ti concentration. The sensitivity increases with Ni content in the alloy. For alloys having greater than 55.0 weight percent Ni, a one weight percent deviation in Ni (or Ti)

concentration will result in approximately a 100°C shift in transformation temperatures. This extreme sensitivity puts a strict requirement on any melting practice to tightly control the Ni and Ti ratio in order to meet the required tolerance in transformation temperatures.

Having close to fifty percent Ti, molten Nitinol is highly reactive and must be processed in vacuum. Both vacuum induction melting (VIM) and vacuum consumable arc melting (VAR) processes are commonly used for production. Other melting processes such as non-consumable arc melting, electron beam melting and plasma melting are also used in experimental scales. In the VIM process, graphite or calcia (CaO) crucible is preferred. Other crucible material such as alumina or magnesia contaminates the molten Nitinol with oxygen. Molten Nitinol does pick up carbon contaminant from graphite crucible. By keeping the melting temperature below 1450°C when using a graphite crucible, the carbon content of a VIM Nitinol ingot can be controlled between 200 and 500 ppm [4]. The transformation temperature can be controlled within +/- 5°C in a VIM ingot. To achieve a more precise control, an in-situ composition control process can be implemented where samples are taken from the molten metal and the transformation temperatures are quickly analyzed for instant composition adjustments [4]. One also needs to bear in mind that because Nitinol transformation temperatures are so sensitive to small variations in chemistry that the analytical methods are not sufficiently accurate to predict the transformation temperature. The transformation temperature in fact correlates much better with the charge chemistry that is used more reliably for ingot formulation [5]. In the VAR process, consumable electrodes of Nitinol are melted and solidify in a water-cooled copper mold. Because there is no contamination from the crucible, cleaner materials with carbon content less than 200 ppm are produced. However, the molten pool of a VAR process is limited to only a small zone. Lacking complete mixing within the entire ingot leads to less homogeneous chemistry and the distribution in transformation temperature when compared to the VIM ingot. Multiple re-melts are required in the VAR process to achieve acceptable homogeneity. Double melting process using VIM primary melting followed by VAR re-melt is used in production with good results. Ingots of 1,000 Kg and 14 inch (35.5 cm) diameter are routinely produced using the VIM/VAR double melt process [5].

Regardless of the fundamental difference between the two melting processes, wires manufactured from VAR and VIM/VAR double melt appear to have similar mechanical and fatigue properties [6].

Metal Fabrication

After melting, the Nitinol ingot is usually forged and rolled into a bar or a slab at elevated temperatures. Extrusion of Nitinol billets and tubes at temperatures between 850°C and 950°C has been experimented [7]. Such hot working processes break down the cast structure and improve mechanical properties. Optimal hot working temperatures appear to be around 800°C where the alloy is easily workable and the surface oxidation in air is not too severe [4]. Following hot working, Nitinol alloys are cold worked and heat-treated to obtain final dimensions with desired physical and mechanical properties.

Cold working of Nitinol is quite challenging because the alloy work-hardens rapidly. It requires multiple reductions and frequent inter-pass annealing at 600-800°C until the final dimension is obtained. Round wires are produced by die drawing processes. Retaining surface oxide, Nitinol wires can be successfully drawn to small sizes. Lubricants successfully used for the drawing of Nitinol wires include sodium stearate soap [8], molybdenum disulfide [9], graphite-containing water based lubricant [10] and oil based lubricant [11]. Following a similar reduction schedule, rectangular wires can be manufactured by drawing round wires while flat wires are typically produced by cold rolling. Comparing to those of rolled flat wire, the dimensions of drawn

rectangular wire are much more tightly controlled. For example, a typical tolerance for the rolled wire is +/-10% while +/-0.0005 inch (0.013 mm) or better is typical for drawn wires. Nitinol tubing although difficult to fabricate is routinely manufactured in commercial scale. Tubes as small as 0.010 inch (0.25 mm) outside diameter are produced by drawing over a non-deformable or a deformable mandrel [12]. Rolled Nitinol sheets with thickness down to 0.010 inch (0.25 mm) and width up to 5 inches (125 mm) are available.

Forming

Because superelastic Nitinol exhibits significant spring-back when deformed in both cold worked and heat-treated states, the alloy is difficult to form at ambient temperatures. Over-deformation of superelastic Nitinol induces martensite and therefore affects the mechanical and transformation properties. Like shape memory Nitinol alloys, if the part is not constrained during heat treatment, the shape will recover partly back to the original configuration. Prototype Nitinol components are normally fabricated by holding the part in a fixture during heat treatment. This process can be scaled up to production quantities by increasing the number of fixture and heat treatment capacity. Semi-automation of this process is also possible by cold forming the part using an automatic forming machine. The formed part is then placed and constrained in a fixture and subsequently heat treated to a desired shape with final properties [4].

Heat Treating

To achieve optimized properties, materials with 30-40% retained cold work before heat treatment should be used. Superelastic Nitinol materials are typically heat treated in the vicinity of 500°C. Lower temperatures in the range between 350°C and 450°C are also suitable for shape memory alloys. Alternatively for alloys with greater than 55.5 weight percent Ni, good superelasticity and shape memory effect can be obtained by solution treatment at high temperatures between 600°C and 900°C and subsequent aging at a temperature around 400°C. This aging process induces precipitation hardening of Ni-rich phases [13]. The transformation temperatures are elevated significantly as the matrix composition adjusts during aging [14].

Machining

Although it is difficult and causes significant tool wear, Nitinol can be machined using conventional techniques such as milling, turning and drilling. Shearing and blanking are quite effective with proper tool design and maintenance. Carbide tools with chlorinated lubricant are recommended for these operations. Abrasive processes such as grinding, sawing and water jet cutting with abrasive particles are successfully used for Nitinol. For example, tips of Nitinol guide wires are commonly tapered by centerless grinding. Laser machining; electro-discharge machining (EDM) and photochemical etching processes are used to fabricate Nitinol components such as stents, baskets and filters. In particular, laser machining has become the preferred process for the manufacture of Nitinol tubular stents. Modern laser cutting machine using a pulsed Nd:YAG laser and equipped with a CNC motion control system offers high speed, high accuracy and the capability for rapid prototyping. Drawbacks are the occurrences of heat-affected zone (HAZ) and microcracks. Managing heat and shape-stability of Nitinol parts is critical and post-processing is required to remove slag, microcracks and HAZ [15]. EDM works well with most Nitinol compositions. A recast surface layer consisting of oxides and contaminants from Cu electrode and dissolved dielectric medium is present and may need to be removed depending on the application [16].

Joining

Welding Nitinol to itself has been successfully performed using CO₂ laser [17], Nd:YAG laser [18], tungsten inert gas (TIG) [19] and resistance welding [20, 21] under Ar or He protective atmosphere. Superelasticity and shape memory effect are generally well preserved in these welding processes. Degradation in tensile strength and the resistance to permanent deformation in fusion zone and HAZ however was noted in particular during CO₂ laser and TIG welding. Nd:YAG laser process, preserving 75% of tensile strength of the base metal and maintaining permanent deformation below 0.2% after a 7% deformation of a superelastic weld specimen, appears to suffer the least thermal degradation. Ti-rich alloys are more susceptible to weld cracking. Using consumable filler metal in resistance welding helps to reduce the risk and significantly increases joint strength [21].

Soldering Nitinol alloys using halogen-based fluxes is described in a US patent 5,242,759. Plating Ni on Nitinol surface improves surface wetting and allows soldering using mild fluxes [20, 22]. Plating a secondary layer of noble metal such as Au further enhances solderability [20]. Ultrasonic solder joint of Nitinol using Sn based solder has also been experimented with good results. Preheat of base metal; ultrasonic power control and proper wetting of the iron tip by the solder are key factors for the success [23].

Joining Nitinol to dissimilar metals is significantly more challenging. Welding Nitinol to stainless steel is especially difficult due to the formation of brittle intermetallic compounds, TiFe and TiFe₂. Using a Ta interlayer, Nitinol has been successfully welded to stainless steel by percussive arc welding [20]. It is anticipated that other welding techniques will also work well for joining Nitinol to stainless steel using proper interlayer materials. With proper design and tooling, mechanical joining techniques such as crimping and swaging offer alternatives that can provide reliable joints between Nitinol and dissimilar metals.

Finishing

Heat treated Nitinol has a typical oxide finish ranging from straw color to blue color. Black color oxide may appear if the processing oxide was not removed during fabrication. These oxide layers can be removed by mechanical means such as grit blasting and polishing. By proper selection of polishing media, a mirror-like finish can be achieved by mechanical polishing. Chemically etching, also effective in removing surface oxide, produces a silver-looking surface. Electro-polishing of Nitinol has also been demonstrated to produce a highly smooth finish.

Corrosion resistance of Nitinol is significantly affected by methods of surface preparation. It is a general belief that preferential formation of titanium oxide on the surface enhances passivity and corrosion resistance. Mechanically polished surfaces, although can be highly smooth, appear to be most susceptible to corrosion attack while the chemically etched surfaces appear to be the most passive [24]. Electro-polishing alone does not sufficiently enhance the corrosion resistance of Nitinol [24]. Passivation following ASTM F86 procedure results in much improved corrosion resistance and biocompatibility [25].

Coating

Ni coating can be deposited onto Nitinol by electrolytic or electroless processes [23]. Other metals such as Au can also be applied electrolytically [26]. There are risks associated with the electroplating process that requires careful controls. Good adhesion and ductility of coating are needed to prevent flaking when deformed to large strains. Damages of coating by either flaking or scratching

may lead to galvanic corrosion. Hydrogen charged into the alloy during plating also needs to be managed to prevent hydrogen embrittlement.

Polymeric coatings are applied by co-extrusion, spray coating or other surface deposition techniques. PTFE is spray coated and cured at high temperatures greater than 300°C which can affect the thermomechanical properties of Nitinol. PTFE films can also be applied by plasma polymerization [27]. Other polymers such as polyurethane and parylene have been applied with good results.

Powder Processes

Various powder metallurgy (PM) processes have been developed for Nitinol on experimental basis. These efforts carry two primary objectives, fabricating near-net shape components and more accurate control of transformation temperatures. Both pre-alloyed powders and elemental powders have been used.

Pre-alloyed Nitinol powders can be fabricated by inert gas atomization [28], hydriding and pulverization [29] or mechanical alloying [30]. The powders are then blended, compacted and sintered. Reported compaction processes include hot and cold isostatic pressing [28], hot and cold uniaxial die compaction [31], direct powder rolling [32] and consolidation by atmospheric pressure (CAP) [33]. Resulting density varies from process to process. While 68% was reported for CAP, 95% density can be achieved by hot isostatic pressing (HIP) [31]. Using a PM process, a proper ratio of two Nitinol powders having known different transformation temperatures are blended, hot isostatically pressed and sintered. A desired intermediate transformation temperature of sintered part can be obtained through this approach with good precision [28].

Alternatively, elemental Ti and Ni powders are blended, pressed and sintered. Nitinol fabricated by injection molding using elemental powders has also been reported [34]. Because the fusion of Ni and Ti is highly exothermic, the heat of fusion can be used to synthesize Nitinol intermetallic. Elemental powders of Ni and Ti can be sintered using either combustion or thermal explosion process. In the combustion mode, the synthesis is ignited by a high temperature source and then propagates through the entire piece. In the thermal explosion mode, compacted powders are heated until an ignition temperature is reached. The fusion energy released at ignition heats up and sinter the material. If the heating exceeds the melting point, a cast structure can result [35]. Otherwise, Nitinol materials sintered from elemental powders are highly porous and may contain other intermetallic phases of Ti_2Ni and $TiNi_3$. Secondary processing such as remelt or extrusion may be required to achieve higher density and improved microstructures [36, 37].

Porous Nitinol has attracted recent attention on its potential as an implant material. Materials with porosity in the range of 30-70% and pore size of 60-100 μm have been synthesized by sintering Ni and Ti elemental powders at temperatures with the presence of liquid phase. Ignition synthesis of porous Nitinol also achieved good results especially with increased ignition temperature [38].

The limitation of Nitinol PM processes appears to be the oxygen content. Sintered Nitinol materials with oxygen exceeding 3000 ppm have been reported [39]. Significant improvement has been achieved in a recent study of a NiTiHf alloy where an oxygen level in the range of 1190-1550 ppm was reported after sintering elemental powders of Ti, Ni and Hf having an oxygen content of 945, 727-948 and 2200 ppm, respectively [40]. Oxygen at these levels may not significantly affect shape memory effect or superelasticity, but may negatively impact ductility and fatigue resistance.

Thermal Spray

Thermal spray is a conventional thick film coating technology. Nitinol coating can be applied by plasma spraying or physical vapor deposition (PVD) [41]. The process has also been used to fabricate Nitinol foils and thin wall mill products [42]. Nitinol foils of 0.5 mm thickness have been successfully fabricated by low-pressure wire plasma spray with subsequent rolling and interpass annealing. The same process has also been used to fabricate tubing of 0.2 mm and 0.76 mm wall thickness with subsequent HIP. Porosity was commonly present in the as-sprayed structure but was eliminated after rolling or HIP. A shift of 13°C in the transformation temperature (A_f) was measured between the wire feed stock and the sprayed foil. While carbon and hydrogen contents slightly decrease during the process, the oxygen content went from 430 ppm for the wire to 1440 ppm for the sprayed foil [42].

Thin Film Fabrication

Nitinol thin film actuators have attracted significant development efforts in the recent past. Nitinol films normally less than 10 μ m in thickness were deposited on silicon, glass or polymeric substrates by sputter deposition. Commercial devices consisting of Nitinol film on silicon substrate are then fabricated by photolithographic techniques [43]. Compositions of Nitinol thin film reported in various studies include binaries in the range of 48.2-51.9 atomic percent Ni [44, 45], NiTiHf [46] and NiTiCu [47] using either pre-alloyed or elemental targets. Deposition using pre-alloyed targets produced films having much more uniform compositions consistent with the target chemistry while the process using elemental targets results in much more difficult control of composition with variations across the film. Films in the as-deposited state are generally amorphous and require subsequent heat treatments to re-crystallize [48]. Crystalline films in the as-deposited state can be achieved with heated substrates [47].

Miniature pneumatic valves actuated by thin film Nitinol are currently being commercialized. Devices such as spacers in flat panel display and other micro electromechanical systems (MEMS) actuated by Nitinol thin film actuators are being developed.

Conclusions

With the rapid growth of the Nitinol industry the associated manufacturing technologies have come a long way in the last decade, although not mature in any standard of metallurgical process. Recent releases of ASTM standards governing material specifications (F2063), standard terminology (F2005) and test methods (F2004 and F2082) not only standardize the language of communication but also promote general consensus within the industry. Significant resources are continuously being invested in process development by the processors as well as the end users. Advancement in Nitinol process development allows the material to penetrate into cost sensitive volume commercial markets. The medical device market can tolerate higher cost but has a strict demand on better quality and consistency. It is anticipated that requirements will continue to pressure tighter chemistry control in raw materials to reliably achieve better than $\pm 5^\circ\text{C}$ tolerance in transformation temperatures. Developments in laser cutting, photochemical etching, forming and surface finishing technologies having potentials to improve physical and mechanical properties, especially the fatigue life will be on-going. Control of surface finish to deliver unfailing corrosion resistance and biocompatibility will receive intense attention for medical implants. While thin film technology is beginning to be commercialized, process stability and quality control of thin film properties will probably attract more awareness. Other near-net-shape technologies such as powder and thermal spray processes may one day find their niches of commercial value.

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