www.medicaldesignbriefs.com

October 2015

MEDICAL DESIGN BRIEFS

Advancements in Photochemical Etching

Nitinol: Superelastic Shape Memory Material

Actuation Technique for Robotic Surgery

SPECIAL SECTION:
Technology Leaders in Contract Manufacturing/Outsourcing

From the Publishers of TECH BRIEFS

An Overview of Nitinol:

Superelastic and Shape Memory

The world population is growing, globalization has resulted in a higher standard of living in many countries, and people are living longer. With increased living standards and choices people make, lifestyle-related illnesses, such as cardiovascular diseases, are on the increase. Companies race to make medical devices to cure challenging physical conditions and diseases. Novel materials are an integral part of supporting such design and development. One such material is Nitinol (NiTi), a serendipitous discovery in 1959 by William J. Buehler during research at the U.S. Naval Ordnance Laboratory, White Oak, MD. Nitinol, which saw use in medical devices beginning in the late 1980s, stands for Nickel Titanium Naval Ordnance Laboratory.

Nitinol is one among many shape memory alloys (SMAs) that have the ability to restore their original shape after deformation. Used in a variety of applications in industries ranging from consumer appliances to automotive to aerospace and medical, SMAs have gained a strong foothold because they offer designers incredible flexibility replacing conventional materials. In medical devices, Nitinol is popular due to its biocompatibility and superelasticity. Nitinol is used to manufacture stents, guide wires, stone retrieval baskets, filters, needles, dental files, and other surgical instruments. (See Figure 1)

The Shape Memory Effect

The most common demonstration of the shape memory effect is that a piece of this metal can be deformed—for example, by winding a piece of straight wire into a tight coil–and then the deformation can be completely removed by heating the metal a small amount, such as dipping it into hot water. As it is heated, the metal instantly "remembers" its old shape and springs back to the form of a straight wire. The shape memory effect is caused when the material undergoes a change in the crystal form as it is cooled or heated through its characteristic transformation temperature. This change in crystal structure in the NiTi alloys is from an ordered cubic crystal form above its transformation temperature (austenite) to a monoclinic crystal phase below the transformation temperature (martensite).

Fig. 1 – Nitinol components are available in many styles—wire, tube, sheet & foil, and machined or formed shapes.

The majority of commercial applications utilize another useful property, which is its exceptional elasticity, commonly referred to as "superelasticity," when one deforms the alloys at a temperature above the transformation temperature. Above the transformation temperature, the material is in the high temperature or austenitic phase. When stress is applied, the deformation causes a stress-induced phase transformation from austenite to deformed martensite. When the applied stress is removed, the material immediately springs back, and the crystal form returns to the austenite phase.

Most NiTi materials are a simple alloy of nickel and titanium with the ratio of the two constituents at about 50 atomic percent each (about 55 percent by weight of nickel). However, subtle adjustments in the ratio of the two elements can make a large difference in the properties of the NiTi alloy, particularly its transformation temperatures, i.e., the temperatures at which the crystal structure of the alloy changes from austenite to martensite or vice versa. If there is any excess nickel over the 50/50 ratio, one sees a dramatic decrease in the transformation temperature and an increase in the austenite yield strength. Increasing the nickel-to-titanium ratio to 51/49 causes the transformation temperature to drop by more than 100°C. This sensitivity of the properties to very small increases in the percent of nickel makes it difficult to manufacture Nitinol of uniform and repeatable properties. But, at the same time, this gives manufacturers a powerful method to control properties and to make ingots of the desired transformation temperature.

In fact, the sensitivity of the transformation temperature to alloy composition is so great that chemistry is not recommended as a way to specify the alloy of interest. Instead, the transformation temperature is a much more accurate means to specify the alloy. One of the most widely used methods of transformation temperature measurement of the ingot is use of a differential scanning calorimeter (DSC). ASTM F2004 is the standard for the DSC test method. The type of transformation information recorded by the DSC is shown Figure 2. The various transformation temperatures are marked.

While the DSC is used for characterizing raw materials, the temperature most frequently specified for the finished product like wires or tubes is the Active Austenite Finish (Active Af) Temperature which is generally determined by a "bend free recovery" (BFR) test. In this test, one deforms a sample of the material after cooling it into the martensitic region and then records the amount of shape recovery that occurs as it is warmed. A graph of temperature versus sample displacement is plotted and used to determine the temperature (Active Af) where the shape recovery is complete. The BFR is a very good functional test that shows distinct shape recovery. ASTM F2082 is the standard for the BFR test method. In most applications, specifying the transformation temperature of the final product (Active Af) is sufficient. However, the transformation temperature of the original ingot may be specified as well, if required.

Superelastic NiTi alloys take advantage of a stress-induced martensitic transformation to achieve incredible amounts of flexibility and kink resistance. For example, alloys that are intended to be superelastic at room temperature are generally produced with their Active Af temperatures just below room temperature, say in the range of 0 to 20°C. Such a material will also exhibit good superelastic properties at body temperature (37°C). Superelastic alloys comprise the largest volume of Nitinol material.

Shape Memory NiTi alloys exploit the ability of the materials to recover a trained shape upon heating above their transformation temperatures. Therefore, the most critical property to specify is the transformation temperature. The Active Af represents the finish of the transformation from martensite to austenite upon heating and, therefore, the temperature at which the shape recovery is complete.

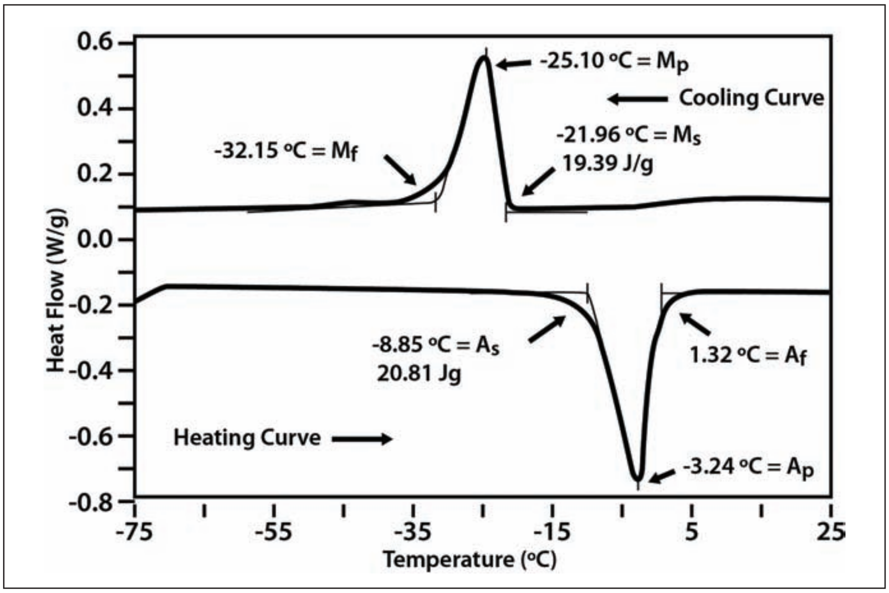

Fig. 2 – Various transformation temperature measurements of the Nitinol ingot are recorded by a Differential Scanning Calorimeter (DSC).

ASTM F2516 is the governing standard for tensile testing of Nitinol. In a typical tensile test, the sample is pulled to 6 percent strain, then unloaded and subsequently pulled to failure. In addition to the ultimate tensile strength and elongation that are common to other materials, there are other critical parameters that are measured when testing Nitinol. When the test is conducted above the Active Af of the sample, upper plateau strength, lower plateau strength and the residual elongation (or permanent set) are also recorded. As the material is subjected to the cyclic test, during loading, the material transforms from austenite into stress-induced martensite and as the sample is unloaded, the material reverses into austenite. Upper plateau is the stress at 3 percent strain recorded during tensile loading and lower plateau is the stress at 2.5 percent strain recorded as the sample is unloaded. Residual elongation is the strain after the load to 6 percent strain and unload is completed. Figure 3 depicts these points.

Processing

Nitinol ingots are melted using combinations of vacuum induction melting and/or vacuum arc remelting. Billets are forged and hot rolled to create intermediate forms which are further fabricated into bars, coils, and plates. ASTM F2063 is the standard that covers the chemical and metallurgical requirements for wrought nickel titanium in such mill forms. Coils are further drawn to make smaller diameter wires and plates are rolled down to make thinner sheet. Bars are gun-drilled to create a "tube hollow", which are then drawn into tubes. Gun-drilling is a necessary evil. It immediately reduces the effective yield of the process as it removes a considerable amount of material that cannot be reclaimed—think bar weight versus tube hollow weight.

Control of oxygen and carbon content in the melt is critical because of the formation of titanium oxides and carbides. These hard inclusions act as discontinuities in the matrix. These have been the subjects of numerous studies on device failure and fatigue strength.

The combination of cold working and heat treatment (thermomechanical processing) is critical to attaining the desired properties in the material. During cold working fabrication operations, such as drawing or rolling, Nitinol alloys work harden very rapidly. If the material is not annealed after a certain amount of cold work, the strength rises to the point where the fracture strength is reached on further deformation and failure occurs.

Heat treatment also used to set the final shape in the Nitinol component. If the Nitinol has a reasonable amount of cold work in it (of the order of 30 percent or more), temperatures of 400° to 500°C with appropriate dwell times will create a straight, flat, or shaped part. The term "shape setting" is commonly used for this process and shaped parts are created using bespoke fixtures. Some common heat treatment methods are strand annealing (for straight wire and tubing), box furnace, molten salt bath, and fluidized bed. Another objective of heat treatment is to establish the final mechanical properties and transformation temperatures in the Nitinol component. After the material has been cold worked, the proper heat treatment will establish the best possible shape memory or superelastic properties in the material while retaining enough of the residual cold work effect to resist permanent deformation during cycling. It also helps to set the Active Af of the parts.

Nitinol tubes, sheets, and wires are subject to a variety of processing operations to make a device. Nitinol responds well to material removal by abrasive techniques such as centerless grinding but is difficult to machine by milling or turning. Laser and electrical discharge machining are common cutting methods for tubing. Additionally, sheet can also be waterjet cut or photo-chemical machined.

Applications

The best known application of Nitinol tube is to make self-expanding stents via laser cutting. It is a popular choice in peripheral vascular applications. Concentricity control and good surface finish of the tube inner diameter is key to good yield when making stents. Nitinol tubes are also used in biopsy, endoscopy, and orthopedics, amongst other applications.

Nitinol guidewires are used to guide catheters into difficult to reach places of the body. They are favorable because they are kink resistant, unlike stainless steel. The wire is elastic and it can follow a tortuous path in the body without damage. Nitinol will rotate smoothly and impart torque. Nitinol wires are also commonly used to make braided stents and filters.

Nitinol sheet is popular because it offers design flexibility not available with other forms—designing products flat and then forming it to make devices. Sheet can be produced with very tight thickness tolerances and uniform thickness control across the surface. This high process capability benefits downstream process optimization and automation—consistent starting sheet thickness, controlled post-processing will yield predictable final dimensions.

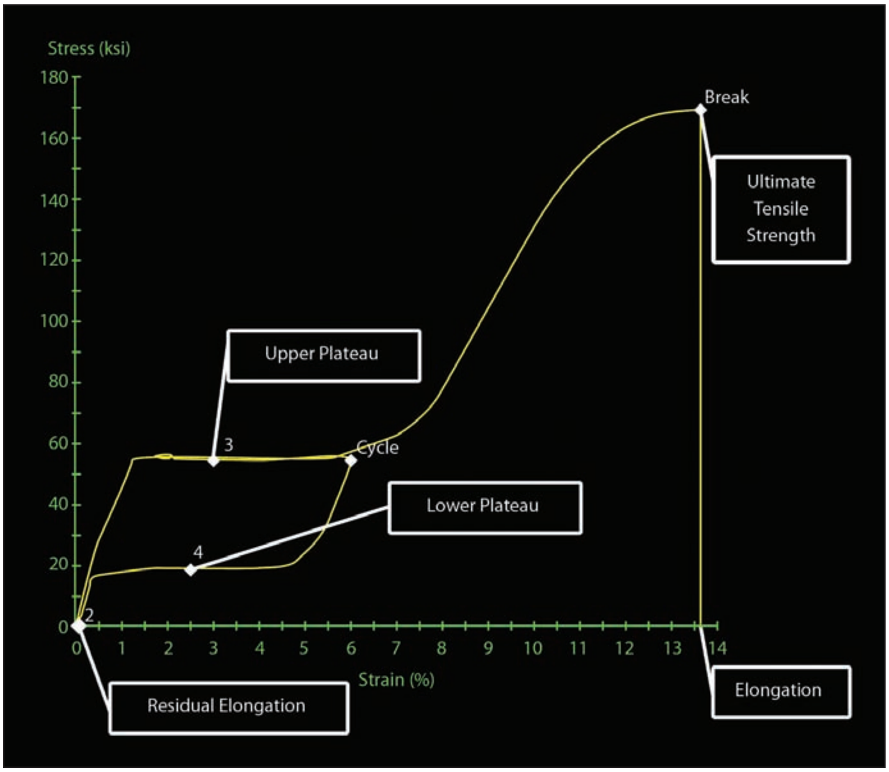

Fig. 3 – Typical Nitinol Tensile Test. In addition to the ultimate tensile strength and elongation that are common to other materials, there are other critical parameters that are measured when testing Nitinol. Upper plateau strength, lower plateau strength and the residual elongation (or permanent set) are also recorded.

One drawback of Nitinol is that it is not radio-opaque, a requirement for proper placement of a stent or the ability to locate the device in the body. Various marking systems made out of precious metals, like platinum and palladium, are commonly used in conjunction with Nitinol-based devices to improve radio-opacity.

Similar to other materials and development programs, close engagement with the supply chain helps the team evaluate cost implications and other engineering challenges early on. When material properties and limitations are well understood and considered, Nitinol can offer a simple, elegant answer to a problem where the previous solutions were particularly complex or expensive.

This article was written by Deepak Kapoor, Nitinol Technology Specialist, Johnson Matthey Noble Metals N.A., San Jose, CA. For more information, visit ***http://info.hotims.com/55594-160***.