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Stent Tubing: Understanding the Desired Attributes

P. PONCIN
MINITUBES, Grenoble, FRANCE

J. PROFT
METALLURGICAL SOLUTIONS, Foster City, California, USA

Abstract

The goal of this paper is to define how stent performance depends on both material properties and physical attributes of the tubing utilized to produce the device. This information will guide stent designers in specifying tubing to achieve the desired device behavior. The "ideal stent" will be presented before comparing existing and candidate stent materials. As a majority of stents are manufactured from metal tubing, the desired tubing attributes are also discussed to demonstrate how they interact with stent performance and manufacturability. The various tube manufacturing methods available to achieve these attributes is also briefly reviewed.

Keywords

Stents, materials, tubing, nitinol, cobalt, stainless steel.

Introduction

New generations of stents are being introduced with claims of improved stent performance based on material properties. As an example, Guidant advertises its new Vision stent with the statement "Vision is laser-cut from a cobalt chromium superalloy that allows us to reduce strut thickness and total stent volume without compromising radial strength or radiopacity. The result? Extraordinary deliverability and the best clinical outcome we have ever had". Similarly, Medtronic describes its Driver Coronary Stent System in the following terms:" Cobalt-based alloy with unique modular stent design. The Driver coronary stent system consists of ultra-thin struts, with the company's proven 10 crown design. The combination of these unique design characteristics provide physicians with the additional flexibility they need for tracking through tortuous anatomy and reaching difficult to access lesions. Because its cobalt-based alloy is denser than stainless steel, the Driver maintains optimal radiopacity."

Several device performance characteristics are indeed directly linked to material. Biocompatibility, X-ray and MRI visibility, radial strength, acute and chronic recoil, axial and radial flexibility, deliverability, profile, and long term integrity, all depend on the materials' mechanical and physical properties. It is therefore of interest to attempt a description of the ideal stent material and to review how various available materials compare to the ideal scenario. This complements earlier papers on this subject [1, 2], which did not attempt to compare various available materials. Given that the most common material format for stents is tubing, a review is conducted to show how tubing attributes influence stent properties and manufacturability.

The ideal stent material

The ideal stent material is fully corrosion resistant, vascular compatible, fatigue resistant, and visible using standard X-ray and MRI methodology. Considerations specific to either balloon expandable or self-expanding stents must also be made.

For balloon-expandable stents, an infinite elastic modulus prevents recoil. A low yield strength is preferred to allow stent expansion at acceptable balloon pressures and facilitates crimping of the stent on the delivery system. High tensile properties after expansion help to achieve radial strength with a minimal volume of implanted foreign material. Higher tensile properties also permit the use of thinner struts for an overall lower profile, thus improving flexibility, deliverability, and access to smaller vessels. A steep work-hardening rate leads to a desirable rise in strength during expansion. Finally, a high ductility is needed to withstand deformation during expansion.

The above properties are interrelated and sometimes contradictory, requiring careful compromise. For example, higher tensile strength materials typically also have higher yield strengths. Although the higher tensile strength is desirable for bolstering radial strength as outlined above, the associated higher yield strength promotes the undesired acute recoil upon balloon deflation. Similarly, a small grain size that is known to favor fatigue resistance and the ability to achieve a favorable polish, usually raises yield strength leading to excessive acute recoil.

In self-expanding stents, large recoverable strains are required for both deployment and crush resistance. This is commonly described as superelastic behavior, with an ideal stress-strain curve showing long and elevated plateaus following an initial elastic loading regime. The device remains within the superelastic range inside the delivery catheter and may again enter the superelastic range after deployment if sufficient deformation is imparted due to vessel interaction or external forces. Elongation and UTS are of significance during stent manufacturing but are given less attention with respect to the superelastic event itself. To the extent that these traditional properties influence fatigue resistance and fracture toughness, elongation and UTS should be regarded as important parameters. Resistance to pulsatile and bending fatigue is of paramount importance, as the stent follows the vessel movements.

The biased stiffness of superelastic nitinol that results from the hysteresis between the loading and unloading path is currently a debated subject. There are arguments in favor of a significant hysteresis to generate resistance to compression and to minimize recoil after balloon deflation. On the other hand, the absence of hysteresis leads to a vessel compliance in terms of crushability/ recoverability similar to the behavior of natural healthy vessels which may minimize tissue damage near the ends of the stent.

Comparing implant grades and other possible metallic materials

Table 1 lists relevant properties for the primary alloys and metallic materials used in permanent implants to date. Other alloys and metals have been added, given that their properties may make them attractive candidates for future stent usage. Several characteristics such as biocompatibility and fatigue resistance of these materials would of course need to be studied which is beyond the scope of this paper. With the exception of the nitinol alloys, the properties listed are for the fully annealed condition, consistent with the desire for high ductility. Properties for three possible variations of nitinol including the commonly utilized superelastic condition, the martensitic condition, and a cold worked version are shown. All materials are non ferromagnetic and therefore MRI safe, but this does not imply that they are free of artifacts. Considerable efforts are underway to evaluate and develop materials that minimize artifacts in order to benefit from the tissue contrast ,the absence of radiation and the possibility to assess blood flow within the stent, which characterize MRI. However, no single material property is known to properly predict artifact free visualization.

Density is reported to illustrate radiopacity as the denser material typically improves visibility. The Elastic Modulus E is key to describe radial strength (a function of E x t, where t is the tubing wall thickness), the resistance to buckling (a proportion of E x t^3) and recoil. UTS and 0.2% Yield Strength are shown to describe the mechanical strength of the material, while their spread is reported to illustrate the slope of the work hardening curve that affects deployment forces and strength of the deployed stent. Break elongation illustrates ductility. Finally, the ratio of Yield Strength to E Modulus is given to characterize the elastic range of the materials, which affects acute recoil and radial strength. The elastic range of nitinol is defined as the maximum recoverable strain and quantifies its superelasticity behavior.

Table 1: Physical and mechanical properties of selected materials.

	DENSITY gr/cm^3	ELASTIC MODULUS G Pa	ULTIMATE TENSILE STRENGTH MPa	0.2% YIELD STRENGTH MPa	UTS - YIELD MPa	ELONG. %	ELASTIC RANGE %
STAINLESS STEELS							
Fe-18Cr-14Ni-2.5Mo "316LVM" ASTM F138	7.95	193	670	340	330	48	0.17
Fe-21Cr-10Ni-3.5Mn-2.5Mo ASTM F 1586	7.90	195	740	430	310	35	0.22
Fe-22Cr-13Ni-5Mn ASTM F 1314	7.88	193	827	448	379	45	0.23
Fe-23Mn-21Cr-1Mo-1N Nickel free SS	7.63	190	931	607	324	49	0.32
COBALT ALLOYS							
Co-20Cr-15W-10Ni "L605" ASTM F90	9.10	243	820-1200	380-780	420-600	35-55	0.16-0.32
Co-20Cr-35Ni-10Mo "MP35N" ASTM F 562	8.43	233	930	414	516	45	0.18
Co-20Cr-16Ni-16Fe-7Mo "Phynox" ASTM F 1058	8.30	221	950	450	500	45	0.20
TITANIUM ALLOYS							
CP Titanium ASTM F 67, Grade 1	4.50	107	300	200	100	30	0.19
Ti-6Al-4V Alpha/beta ASTM F 136	4.43	105	860	795	65	10	0.72
Ti-6Al-7Nb Alpha/beta ASTM F1295	4.74	106	1000	900	100	12	0.85
Ti-15Mo Beta grade ASTM F2066	4.95	83	793	655	168	22	0.79
REFRACTORY							
Tantalum	16.60	185	207	138	69	25	0.06
Niobium	8.57	103	195	105	90	25	0.10
Tungsten	19.3	411	3126	3000	126	3	0.73
Molybdenum	10.2	324	1540	1386	154	15	0.43
PRECIOUS							
Pt-10Ir	21.55	150	340	200	140	25	0.13
NITINOL							
Martensitic	6.45	40	1200	200-300	900-1000	25	1.9
Cold worked 40%	6.45	40	1450	NS	NS	12	4-6
Superelastic	6.45	90	1400	NS	NS	14	6-8
MAGNESIUM							
Mg-3A1-1Z	1.8	45	255	162	93	10-25	0.36

316L stainless steel is a reference for successful stent applications, despite a weak radiopacity. Nitrogen enriched and nickel free (by manganese substitution) stainless steel grades achieve significantly higher strength while the other properties remaining very similar. In addition, the Mn-Cr austenitic stainless steels eliminate the concern with allergic reactions to nickel.

The cobalt based alloys exhibit comparatively higher density, E modulus, strength, and difference between yield and UTS, but a similar ductility when compared to stainless steel. Within the Co-Cr family, these properties are the highest for L605. Given current interest in this alloy as a stent material, and the fact that stainless steel has been the workhorse material of balloon expandable stents,
a closer examination of the behavior of these two alloys was conducted.

Figure 1 and Table 2 show tensile test results for annealed L605 and 316L. Samples were pulled to 30% strain, a typical value during stent expansion. The specimens were then unloaded to determine spring back characteristics and reloaded to failure. Acute recoil derives from the spring back and is a function of the E modulus and the stress at 30% strain. The results show higher recoil for L605, despite its stronger modulus.

Additional observations from the same tensile tests offer an interesting perspective regarding radial force. Radial force depends on the flow stress after expansion. It is interesting to note that the stress at 30% strain for L605 is 66% higher than the stress at this same strain level for 316L.

Finally, consider the slope of the curves in the stage following the yield point where strain hardening is occurring. L605 strengthens at 15 MPa / % strain, versus 9.6 with 316L. With a rapidly increasing flow stress, localized strains will tend to propagate across a strut length, as the initial deformation site strengthens rapidly. To the contrary, materials with a shallower slope will tend to localize deformation at areas of stress concentration.

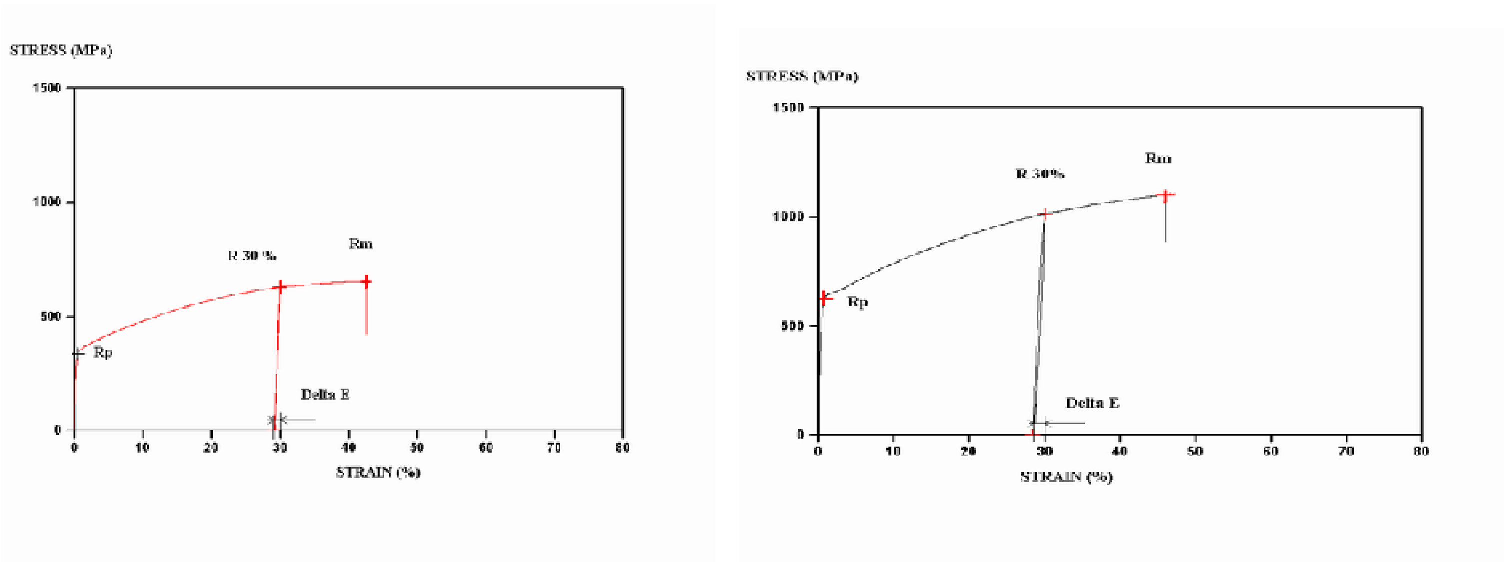

Figure 1: Comparative tensile testing of annealed 316L and L605 tubing. Samples are pulled to 30 % strain and then unloaded to reveal spring back behavior. Samples are subsequently reloaded and pulled to rupture.

Table 2 : Comparative tensile test results on annealed 316L and L605 tubing

	316L	L605	?%
Rp : Yield Strength at 0.2% offset (MPa)	366	629	+72
R 30 % : Stress at 30% strain (MPa)	655	1089	+66
Rm : Ultimate Tensile Strength (MPa)	675	1147	+70
Delta E : Spring back after 30% strain	0.34	0.45	+32
Ductile loading slope (MPa / % strain)	9.63	15.35	+59
Elongation (%)	43	46	+7

To this date, the titanium family has not been used in stents, despite its excellent reputation as a biomaterial and its good MRI visibility. Usage has been hindered by the low density, elastic modulus and strength of pure titanium. The alloyed alpha-beta grades increase strength but negatively affect elongation. In addition, the combination of higher strength with a low modulus increases the elastic range; hence recoil, without reaching a sufficient recoverable strain to permit self expandable usage. There may be some potentially interesting beta or near- beta titanium grades with improved density, ductility and strength. Their high strength and elastic range have found orthopedic and orthodontic applications.

Refractory metals such as tantalum and niobium have been used in stents, tantalum being of particular interest for combining high radiopacity and good MRI visibility. Note also that tantalum shows the smallest elastic range among all materials in Table 1 which would help minimize recoil. Tungsten and molybdenum are also included in Table 1 to show their remarkable E modulus and strength. Note as well, the very high density for tungsten. Although their usage as pure metals is not envisioned for stents, their properties as alloying elements are promising. Several of these refractory metals are beta titanium stabilizers. Finally, refractory metals show minimal MRI artifacts.

Pure precious metals are mechanically rather weak, but platinum-10% iridium has been utilized in a stent application. A 20% iridium content or alloying with tungsten can further increase strength significantly for a similar ductility. Platinum, iridium and gold’s exceptional density make them materials of choice for improving the radiopacity of other alloys, which has been reported for nitinol [4] and stainless steel [5]. A palladium based alloy has been described [6] as minimizing MR artifacts, with an improved radiopacity and a similar strength when compared to stainless steel.

The nitinol family can be split into three categories displaying radically different mechanical properties. Balloon expendable stents have been designed from martensitic nitinol, either to use the shape memory effect for retrieval of a temporary stent by contracting it upon heating [7], or as a regular balloon expandable stent, advocating exceptional flexibility thanks to the long and low initial stress/strain plateau of martensitic nitinol [8], followed by a very steep work hardening curve. Superelastic nitinol is the material of choice for slotted tube self expanding stents due to the remarkable recoverable strains of up to 8%. Its thermo-mechanical properties can be modified by the processing parameters, by altering the nickel/titanium ratio, and through the addition of ternary elements [4, 5, 9]. All of these can affect radiopacity, strength, hysteresis and transformation temperatures.
Cold worked nitinol exhibits an amazing Hookian-like elasticity, permitting large recoverable strains of up to 4 to 6%. The UTS is quite high, with a similar ductility to superelastic nitinol. Its properties are not temperature dependant. Such exceptional features may generate some creative designs.

A common magnesium industrial alloy is the last material displayed. The corrosion behavior of magnesium based alloys is the source of current research on bioabsorbable stents [10]. However, the material density and mechanical properties are very low compared with any currently used stent material.

Finally, as no available material is known to demonstrate all the ideal features, compromises have to be made in which some properties may be sacrificed for others. For example, nitinol stents are made from a rather low ductility material, with a break elongation typically less than 15%. Yet adequate design permits amazing expansion ratios without rupture. Creative alloying is another promising path to tailor the material properties to the specific requirements of vascular implants. An example is the radiopacity enhancement by addition of dense elements already mentioned.

The desirable tubing attributes

A majority of stents are cut from tubing. Besides the intrinsic material properties previously discussed, several tubing attributes can significantly influence stent performance and its manufacturability. The important desirable tubing attributes are now described.

The selection of a melt source is extremely important. The nature and purity of the elemental material components mixed prior to melting, together with melt practice itself, have an influence on homogeneity, porosity and microcleanliness of the cast alloy.
Although the ASTM and ISO standards set limits, these are often not sufficient to bring the required safety in a stent application.
This is particularly the case with regard to microcleanliness. Take stainless steel as an example wherein both ASTM F138 and ISO 5832-1 permit heavy inclusions up to a rating of 1, allowing inclusions as thick as 15 µm on a 75 µm length. Such defects are massive when compared with stent struts that can be thinner than 100 µm. Such inclusions represent a serious threat for rupture upon expansion and of premature fatigue failure. Inclusions become even more significant with the reduction in strut dimensions that come with the current trend towards stronger materials and small vessel stenting. When selecting a material source, attention should also be paid to chemical composition homogeneity and its consistency across heats will favor uniform mechanical properties and electropolishing response.

Tubing is typically produced in either welded-redrawn or seamless form. Despite the robustness of modern welding equipment and continuous on line inspection systems, it is not possible to guarantee a fully defect free weld without localized micro-contamination and segregation. Traces of lubricant on the strip are enough to cause irreversible carbon enrichment in the molten material leading to unacceptable risks of corrosion and embrittlement. Therefore, the tubing utilized for stents and other implantable devices should be seamless.

Next, an adequate degree of control in the tube drawing process is required to ensure repeatable properties for the tubing. While stainless steel exhibits a moderate sensitivity to processing parameters, L605 and nitinol are more difficult to control and can show wide ranges in their properties, depending on processing. This sensitivity gives an opportunity to tailor the material properties to the device requirements, provided that the tubing manufacturer understands the detailed material behavior and tightly controls his process.

L605 is very sensitive to heat treatment conditions. A study on annealing of 35% cold worked tubing was conducted utilizing the time and temperature ranges advised by the alloy supplier. Time was varied between 2 and 20 minutes and temperature from 1100 to 1200°C. Tensile test results and microstructure examination have shown wide variations in the following ranges: UTS 819 - 1117 MPa; 0.2 % Yield Strength 380 – 648 MPa; elongation 35 – 56%; Grain diameters 5.6 – 89.8 µm.

An additional complexity with nitinol resides in the interaction between the as-delivered tubing and the thermo-mechanical stent shape setting. Moreover, a given set of tubing properties can be achieved through different combinations of process parameters, like cold work and heat-straightening. Such apparently similar tubing lots may react differently through the stent shape setting operations. This makes an argument to specify tubing properties after a defined thermal post-processing rather than as drawn. Also, it can be noted that stents cut from large tubes only need a single shape setting step with minimal deformation and limited thermal exposure. This approach provides the opportunity for a more uniform and controllable structure than those expanded in multiple steps from small tubing. A previous paper [11] gives a detailed comparison of these alternative nitinol stent manufacturing routes.

Microstructures with uniform and equiaxed small grains are generally preferred for polishing and for resistance to fatigue and corrosion [12]. Again, the ASTM and ISO standards have set limits that are not optimal for stents. An often specified limit of ASTM Grain Size 5 corresponds to a grain diameter of 63.5 µm that could lead to a single grain through the wall for the thinnest stents, an obviously unacceptable situation. Minimizing grain size may not be the ultimate objective though, as it also interferes with the mechanical properties and polishing. It will typically raise the yield strength with negative consequences on recoil at crimping and upon expansion. Here again, a compromise needs to be found.

Dimensional accuracy is key to stent performance and manufacturability. Wall thickness consistency is needed for an even deployment of the stent. It is of utmost importance in the laser cutting to achieve a consistent strut width. If the constant laser beam energy hits variable walls, it will tend to cut a wider slot where the wall is thinner and may damage the opposite side of the tubing. The accuracy of the cut stent depends on the ability of the tube manufacturer to hold the smallest variability and to minimize the offset between mean and nominal dimensions for which the laser set up has been optimized. . Wall should be specified with tolerances and a concentricity requirement. Note that minute tolerances imply an adequately accurate wall measurement system, with a preference for hard contact gages over optical systems. The outside diameter (OD) plays a major role in the guidance of the tubing under the laser beam. Narrow tolerances and tight cylindricity favor the laser cutting accuracy.

Surface finish should be compatible with obtaining the desired stent finish after the cleaning and electropolishing steps. These operations differ among stent manufacturers, depending on the amount of material removal targeted by the respective process. This results in different surface requirements on the raw tubing. The ID surface is usually more critical, as it sees less material removal than the OD. Finish is typically specified by surface toughness (Ra) and by limits on defects such as draw marks and scratches that can be defined through visual standards setting the acceptance limits.

Dimensional accuracy and surface finish vary greatly with the tubing process and the type of alloy being drawn. Figures 2 and 3 illustrate the various drawing processes. Whenever compatible with the material, dimensions, and temper, the floating and fixed plug drawing process bring the best geometry and surface. Hard mandrel drawing is an alternative that is often employed when plugs do not practically work. This is often related to the behavior of the tool / material interface where some alloys tend to stick and gall. Some materials including nitinol need an oxide layer as a lubrication support. This layer has a low ductility and may crack under the stresses imposed by drawing and thermal treatment. Unless properly controlled, these cracks can propagate in the bulk material with devastating effects. The oxide layer can be removed from the ID and OD by polishing or etching. However, a majority of stent cutters prefer to keep oxide on the ID as they have found that the laser generated slag can be easier to remove. The ductile core drawing technique is also used. In this technique, a mandrel is introduced into the tubing blank and remains inside it through the succession of draw passes and anneals. It is removed by stretching at the end of the process. In ductile core drawing, the wall accuracy depends on the consistency of the ductility for both the tubing and the mandrel. It does not usually provide the same degree of accuracy achieved with hard tool techniques.

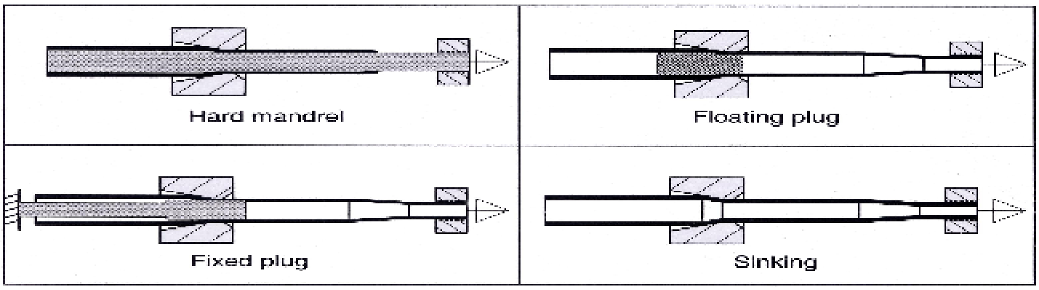

Figure 2: Hard tools drawing techniques: OD, ID and wall result from the contact with rigid tools which do not deform during drawing.

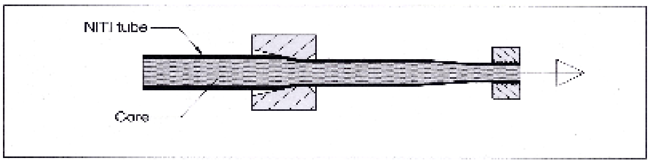

Figure 3: Ductile core drawing: ID/OD ratio remains constant.

Finally, although a fully annealed condition is the norm on the stent itself, cold worked tubing can be preferred during laser cutting, followed by an annealing step on the stents later in the process. This approach helps prevent handling damage to the fragile annealed tubing and the post cutting anneal can help release residual stresses generated during laser cutting. The final anneal needs to be carefully controlled to obtain the desirable mechanical properties and microstructure.

Conclusion

The properties of a wide selection of metallic materials have been described and discussed, in relation with ideal stent material features. It was then shown how tubing attributes influence stent performance and manufacturing, giving a basis for designers to properly specify the desired tubing parameters.

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