Comparing and Optimizing Co-Cr Tubing for Stent Applications

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Abstract

The properties of cobalt-chromium alloys which have recently been introduced in several new generations of vascular stents will be reviewed. Physical and mechanical properties of L605, MP35N and Phynox/Elgiloy are compared and discussed in relation to stent performance. With a higher elastic modulus and density, L605 stands out as a preferred stent material and its behavior is further investigated. Tensile data and microstructural observations are presented for tubing with various amounts of cold work annealed at a variety of temperatures. It is shown that although material properties can be adjusted over a wide range, optimization of stent performance can be achieved with tight control of tube processing parameters.

Introduction

Cobalt-Chromium alloys have a long history as implant materials in dentistry, orthopedics and cardiology. Prior applications inlvolving blood contact are found in pacing leads, vena cava filters, AAA stent grafts and self-expanding stents. The driving force for the selection of these alloys has been the remarkable combination of an acceptable biological response with very high strength in the cold worked condition.

The use of Cobalt based alloys in balloon expandable stents is rapidly growing as exemplified by six companies promoting such products in the 2004 Euro-PCR Materials Catalog [1], while none did two years earlier. In opposition to the other Co based vascular products mentioned above, the material is used in the annealed condition to facilitate plastic deformation during stent expansion.

Co-Cr Alloys and Stent Performance

An earlier paper [2] describes the ideal balloon expandable stent material and compares selected alloys properties. In summary, Co-Cr alloys exhibit a high density that favors radiopacity, a high elastic modulus limiting recoil, and strong tensile properties allowing stent designs with thinner struts. This permits a lower profile, smaller stent volume and improved flexibility/deliverability with access to smaller vessels. All of these performance improvements are claimed by the companies that have introduced new generation stents using Co-Cr alloys.

The favorable influence of smaller strut thickness on long term clinical outcome is discussed by Lau et al [3], based on the ISAR-STEREO study [4] and on work by Briguory et al [5] on small vessel stenting.

Table 1: comparing Co alloy stents with previous 316 stainless steel generation from the same company and with current leading stainless steel stents [6].

Company	**Co-Cr Alloy Stent**	**Previous Stent**	**Co -Strut Thickness (µm)**	**316L Strut Thickness (µm)**
New Co-Cr Stents and previous 316L Generation				
AMG	Arthos Pico	Arthos	65	125
B.Braun	Coroflex Blue	Coroflex	65	91
Eurocor	Genius Megaflex	Megaflex	N/A	110
Guidant	Multilink Vision	Multilink Zeta	80	91 / 124
Guidant	Multilink Mini Vision	Multilink Pixel	80	99
Medtronic	Driver	S7	91	100 x 127
Medtronic	Micro Driver	S660	91	127 x 152
Market leading stents, 316L				
Boston Scientific	Express II			132
Cordis	Cypher			140

Table 1 illustrates the significant decrease in stent strut thickness that comes with the transition from stainless steel to Co alloys. These newer stents also all show thinner struts than the current market leading stainless steel stents.

Comparing Co-Cr Alloys

The main alloys used in balloon expandable stents are commonly known under the commercial names of L605, MP35N and Phynox / Elgiloy. Table 2 shows the designation and standards that cover these materials while Table 3 displays selected physical and mechanical properties that are typical of annealed tubing material for stent application.

Table 2: Designation and standards for Co-Cr alloys used in stents.

Common Name	ASTM Material Designation	UNS	ASTM	ISO
MP35N	35Co-35Ni-20Cr-10Mo	R30035	F562	5832-6
Phynox	40Co-20Cr-16Fe-15Ni-7Mo-	R30008	F1058	5832-7
Elgiloy	40Co-20Cr-16Fe-15Ni-7Mo-	R30003	F1058	5832-7
L605	Co-20Cr-15W-10Ni	R30605	F90	5832-5

Note that Phynox and Elgiloy are described as two grades within the same ASTM and ISO standards. In practice, ingots are often melted to obtain a chemical composition that satisfies both grades.

Table 3: Selected physical and mechanical properties of annealed Co-Cr alloys and 316L stent tubing.

Alloys	**Specific Mass (g/cm^3)**	**Elastic Modulus (GPa)**	**UTS (MPa)**	**Yield Strength (MPa)**	**Tensile Elongation (%)**
316 L	7,95	193	670	340	48
Phynox / Elgiloy	8.30	221	950	450	45
MP35N	8.43	233	930	414	45
L605	9.1	243	1000	500	50

The mechanical properties are typical values obtained after cold work and annealing in order to obtain a small grain size of ASTM 7 or finer. The requirement for fine grain size is even more important with these materials, as the strut thickness decreases. A usual rule of thumb calls for a minimum of 3 grains through the strut.

The density, elastic modulus and mechanical properties are clearly higher than those of 316L for the three Co-Cr grades.

These alloys are non ferromagnetic and therefore MRI safe. Artifacts have been shown to be lower with Co-Cr stents than with stainless steel [7].

While the tensile properties of the 3 alloys appear comparable, L605 stands out with its higher density and stronger elastic modulus, bringing a comparative advantage in stents for radiopacity and recoil. This alloy's properties will be now further investigated.

Optimizing L605 Properties for Stent Performance

<u>Material properties and stent performance:</u> L605's sensitivity to processing parameters has already been described [2]. This imposes a need for strict control during manufacturing to ensure repeatable properties. It is also an opportunity to tailor these properties to stent design in order to optimize the device performance. Several papers have discussed the link between stent design and its performance [3,8,9]. Consequently, optimized material properties are dependant on the device design. For exemple, a stent design that concentrates strut deformation on flexible hinges with low recoil will probably want to maximize both yield strength and UTS. However, alternative designs concerned with recoil will seek a lower yield strength. As a result, it appears necessary to describe the range of achievable properties to permit stent designers to choose the optimal set of properties for their particular design.

<u>Experiment</u>: An L605 hot rolled hollow at 30 mm OD x 3 mm wall was cold drawn into 2.0 mm OD x 0.12 mm wall tubing and annelead at 1150°C. Samples were further cold worked in a series of cross-section reductions ranging from 4% to 45% and then annealed at 4 different temperatures: 900, 1000, 1100 and 1175°C for 10 minutes. Sample of each condition were characterized by metallographic examination and tensile testing.

<u>Results:</u>

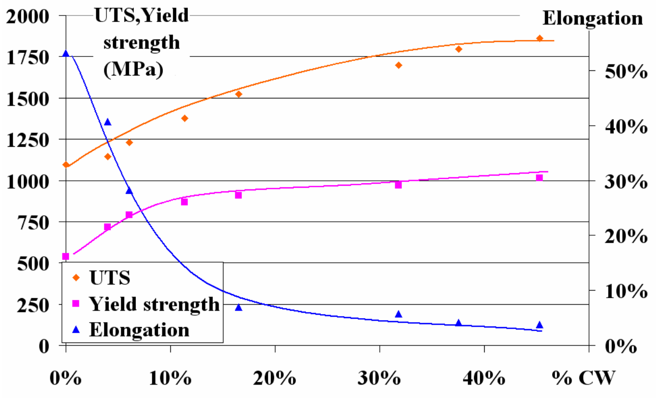

Figure 1: Mechanical properties vs. cross-section reduction

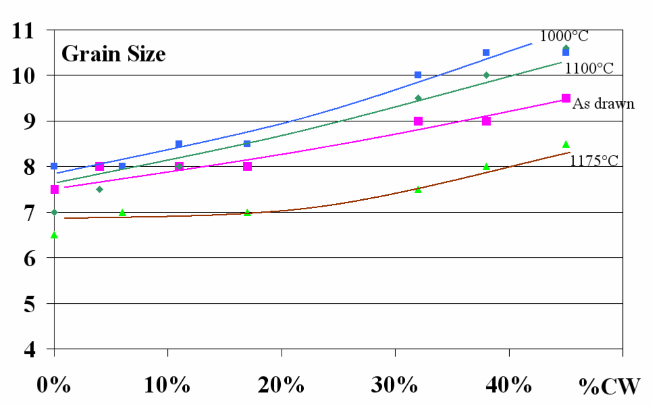

Figure 2: Tubing grain size vs. Cold work + different anneal temperatures

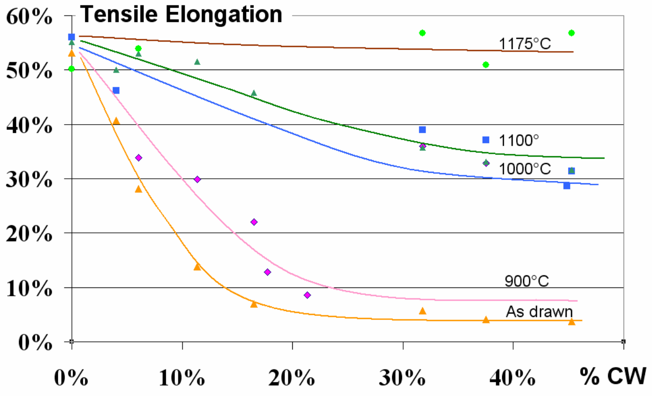

Figure 3: Tensile elongation vs. cold work + different anneal temperatures

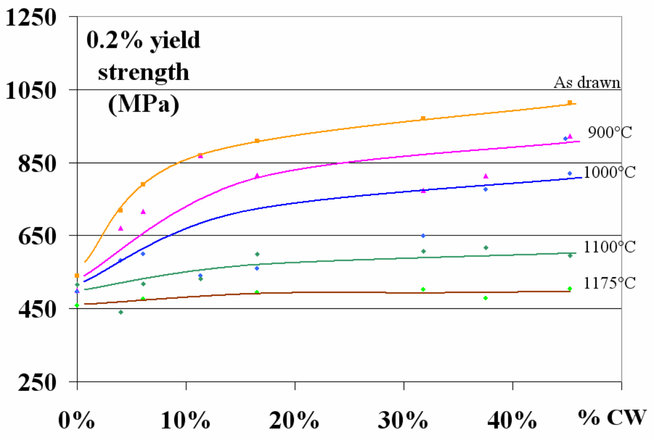

Figure 4 : 0.2% yield strength vs. cold work + different anneal temperatures

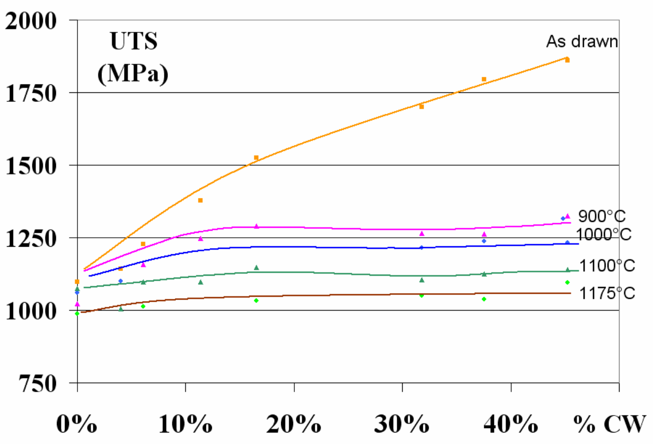

Figure 5: UTS vs. Cold work + different anneal temperatures

Discussion: In a balloon expandable stent, requirements typically involve a minimum elongation of 35% and grain size of 7 or finer. At 900°C, the results are very close to those measured in the as-drawn condition, recristalisation has not been initiated and elongation is not sufficient. At 1175°C, grain growth becomes the limiting factor. Within these limits, the data permits the choice of an optimal set of properties with the corresponding processing parameters. Compared with 316L, the range of properties compatible with stent use appears wider.

In Fig. 1, L605's mechanical properties response to cross-section reductions appears similar in behavior to stainless steel and other austenitic alloys for elongation and UTS. The slow increase in yield strength with section reductions above 15% is attributed to the mode of cold drawing from the original 2.0 mm diameter. The tubing was reduced by sinking, with an unsupported ID, which changes the dislocation distribution when compared with mandrel or plug drawing .

Figure 2 shows a standard response of the microstructure to thermal and mechanical actions. Grain size decreases with higher cold work and annealing temperature. Grain refinement begins at 1000°C for a minimum cold work of approximately 20%. Grain growth becomes significant between 1100 and 1175°C, getting close to the usually specified limits with the higher temperature for tubing with lower cold worked .

The material exhibits a high ductility for annealing temperatures commencing at 1000°C. It decreases with higher cold work when annealing at 1000 and 1100°C . At 1175°C, elongation remains around 55% independant of the cold work.

Figure 4 shows the decrease of yield strength with higher annealing temperatures and the influence of cold work with annealing temperatures under 1100°C. Note the steep work hardening slope of the material in the as-drawn condition.

The results exhibited in Fig. 5 show that the UTS behaves in a similar fashion to yield strength, but with a lower sensitivity to the processing parameters.

All measurements have been performed on annealed tubing with the exception of the as-drawn specimens. They represent values that can be obtained on stents that are annealed after beeing cut from the cold worked tubing. When annealing is performed on the tubing, it needs to be followed by a straightening operation in order to be loaded on the laser cutting machines. Straightening affects the mechanical properties, and in particular raises the yield strength, due to the steep work hardening slope of this material. Separate experiments have shown a typical increase of 15% for the yield strength , with only minor effects on UTS and elongation (<5%).

L605 microstructure

The microstucture of L605 has been studied through optical microscopy and scanning electron microscopy (SEM) at various stages of the tube drawing sequence.

The original hot rolled hollow was found to display heterogeneous grain size through the section with an ASTM size of 4 to 5 in the core followed by a layer of finer size 6 grains and an external band with large size 3 grains. The grains appear twinned with the presence of nodules located within the grains and at the boundaries, as shown on Fig. 6 and 7.

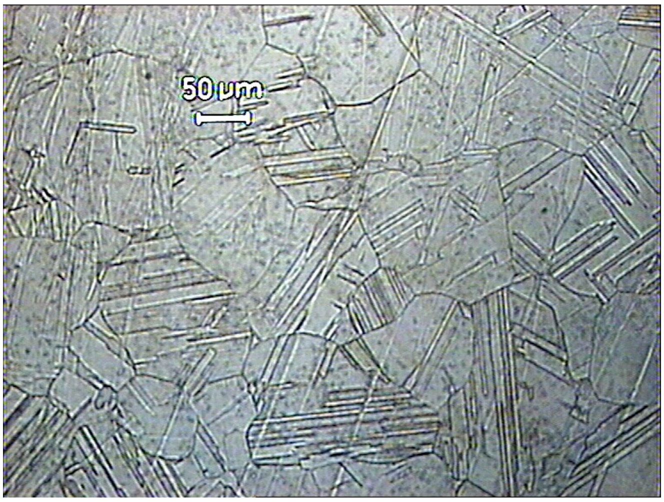

Figure 6: Twinned austenitic grains in the hot rolled hollow.

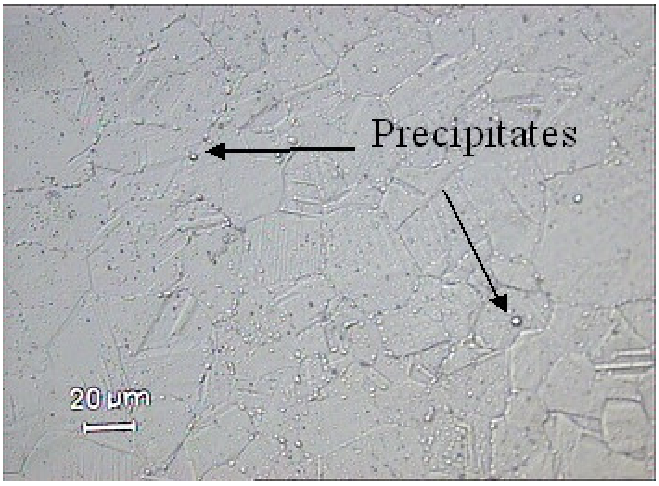

Figure 7: SEM observavation on the hot rolled hollow.

Grain size reduces quickly through the sequence of cold drawing and annealing, while the size uniformity improves. The final stent tubing size is typically achieved after 15 cycles and exhibits a uniform distribution of fine equiaxed grains, whose size depends on the processing parameters as shown earlier in Fig. 2. However, grain growth observed after an 1175°C annealling shows more heterogeneity, suggesting a coalescence mode of grain growth.

In Figs. 8 and 9, SEM examination on finished tubing shows an even distribution of spherical nodules with diameters up to 1 µm. An EDS analysis on a nodule has identified a high tungsten content. Further work is required to understand the exact chemical composition of these nodules, their generation and dissolution modes, and their influence on the mechanical properties of the tubing.

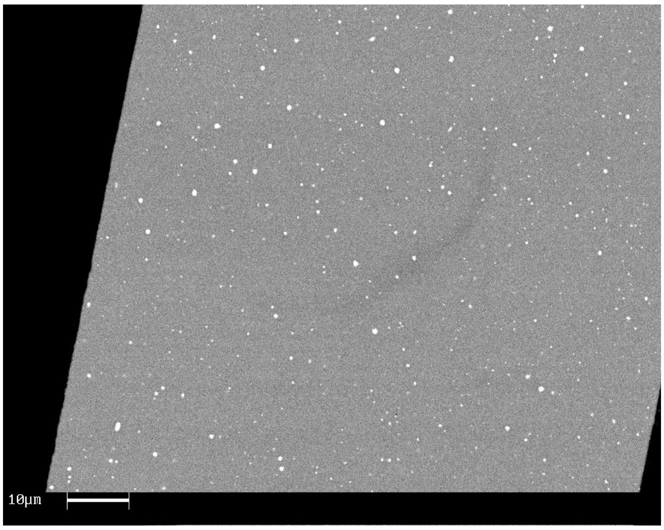

Figure 8: SEM image on polished sample of stent size tubing

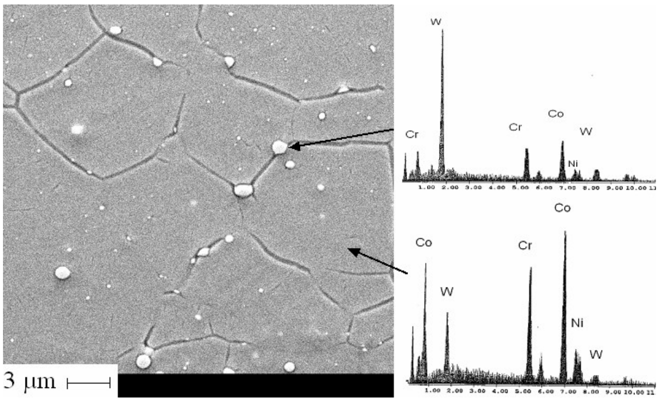

Figure 9: SEM image after etching showing tungsten rich nodules up to 1 µ

Summary and Conclusion

The introduction of Co-Cr alloys in a new generation of stent has enabled a reduction in strut thickness, which has been shown as a positive factor for clinical performance.

Selected material properties influencing stent performance have been reviewed for L605, Phynox / Elgiloy and MP35N.

With a higher density and elastic modulus, L605 appears of particular interest. Experimental results are showing the range of properties achievable on stent size tubing. Their dependence on cold work and final anneal temperature is described for a cold work range of 0 to 45% and a temperature window of 900 to 1175°C. This allows stent designers to select the optimal material properties for their device

The wide range of material properties requires a tight control of the cold work and annealing during tube and stent manufacturing. The particular influence of tube straightening has been discussed.

Finally, the material microstructure is described, showing twinned austenitic grains which remain uniform in size after cold work and annealing at low and moderate temperatures. Small tungsten rich nodules are shown within the microstructure.

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