Composite wire with enhanced radiopacity, elasticity, and electrochemical behavior

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Background

Seeing is believing and for many life-saving medical devices, seeing is succeeding. Minimally invasive surgical procedures in which devices are delivered to the target site via guidewires and catheters often rely on real-time imaging methods such as fluoroscopy to enable accurate placement and ensure proper deployment (1). To be distinguished from fluoroscopic image background, devices must have a certain amount of radiopacity, or ability to block and scatter x-rays. Radiopacity is thus an important property and can be challenging to achieve in thin material sections. Radiopacity is largely a function of three things: section thickness, material density, and material atomic number. For small devices like stents with very thin struts (e.g. 0.3 to 0.02 mm), proper material selection is required to account for lack of section thickness. Deductively, from Table 1, material selection can have a large impact on device radiopacity. Platinum, for example, has nearly 5 times the density of titanium, and 12 times the density of magnesium. Nitinol, being roughly half titanium, also has relatively low density compared to stainless steel, cobalt chrome, tantalum, or platinum.

Table 1. Material properties of medically relevant metals

Alloy	Density (g/cc)	Major Element Atomic Number
Mg	1.74	12
CP Titanium	4.5	22
Nitinol	6.45	28/22
Stainless Steel	7.87	26
Cobalt Chrome	9.13	27
Tantalum	16.65	73
Gold	19.3	79
Platinum	21.45	78

Several strategies have been employed to achieve adequate combinations of radiopacity, mechanical strength, biocompatibility, and cost. Some devices achieve sufficient radiopacity without specific enhancements. Other devices will incorporate radiopaque (e.g. Pt, Ta, Au) markers as secondary add-ons (2), or as a portion of the wires of a multi-wire construct. In some cases, alloy compositions can be tuned to enhance radiopacity with additions of radiopaque elements (3) (4) (5). An increasingly common strategy to improve radiopacity of an entire device without the need to modify alloy compositions or add on secondary markers is to use a DFT® composite wire produced by Fort Wayne Metals.

DFT® wire is a composite structure with a core of one material and a shell of another. This can be used to produce wires which advantageously combine the properties of two or more materials. Generally speaking, these DFT wires are produced and used in sizes ranging from 0.01 mm up to 1 mm. The most prominently used case is a 35N LT®-DFT-Ag wire for biostimulation leads, where the cobalt-chrome 35N LT alloy shell provides strength, fatigue resistance, and corrosion resistance, while the Ag core provides conductivity. An increasingly used construction is NiTi-DFT-Pt. The superelasticity of Nitinol is truly a lifesaving property, enabling minimally invasive devices which couldn't be delivered with other

Keywords: radiopacity, radiopaque, x-ray, wire, composite, platinum, magnesium, Nitinol, powder

materials. As can be inferred from the data in Table 1, Nitinol also has relatively low radiopacity. The addition of the Pt core provides radiopacity with minimal impact on mechanical performance at low core ratios. At high core ratios, however, the Pt can become an impediment to the full superelastic performance of the Nitinol due to plastic deformation resisting full recovery (6).

The material in Table 1 with the lowest density is magnesium, a nutrient metal being used in absorbable devices. As can be deduced from Table 1, the radiopacity of Mg is very poor, rendering Mg stent struts invisible in most x-rays (7). While incorporation of a radiopaque metal core (e.g. Mg-DFT-Pt, Mg-DFT-Fe) is technically feasible, the resulting galvanic coupling between the Mg and the more noble metal core will lead to rapid dissolution of the Mg.

As the preceding paragraphs explain, wire radiopacity is an important aspect of stent design and can be enhanced through DFT wire compositing. However, this approach can have negative mechanical impacts in Nitinol wire and negative electrochemical impacts in magnesium wire. An improved solution would offer the radiopaque enhancements without the drawbacks of the dense metal core.

A new development

Fort Wayne Metals has recently invented and continues to develop a new class of wire composites with radiopaque powder cores (Figure 1). This patent-pending technology provides radiopaque enhancement like tantalum and platinum without a mechanical or electrochemical penalty.

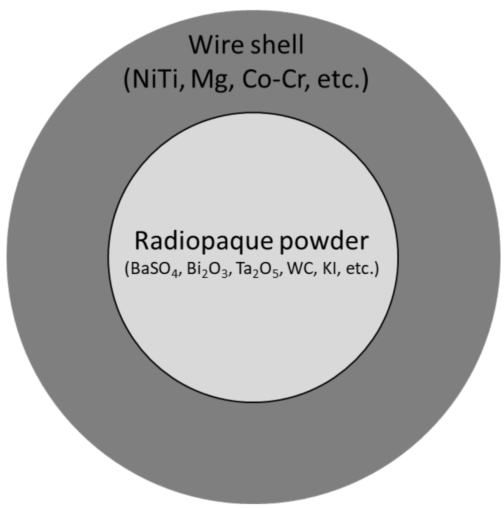

Figure 1. Conceptual cross-section of a radiopaque powder core DFT wire.

Promising powders include bismuth trioxide, tantalum oxide, and tungsten carbide, though many types could serve this radiopacity-enhancing function. Other potential powders include barium sulfate, zirconium oxide, hafnium oxide, titanium oxide, niobium oxide, strontium oxide, zinc oxide, rare earth oxides (e.g. erbium oxide, holmium oxide, gadolinium oxide, dysprosium oxide, ytterbium oxide, and neodymium oxide), iodine or iodine-based compounds (e.g. potassium iodide), bromine or bromine-based compounds (e.g. sodium bromide, potassium bromide), among others. Other suitable powders may be found in other references (8) (9).

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Powder cores are suitable in shells of nearly all wire alloy classes discussed above, and these shells may include magnesium, zinc, iron, titanium, titanium-beta, Nitinol, stainless steel, cobalt-chrome, nickel, tantalum, platinum, tungsten and alloys thereof.

The following sections will highlight working examples and quantify mechanical and radiopaque properties.

Keywords: radiopacity, radiopaque, x-ray, wire, composite, platinum, magnesium, Nitinol, powder

Powder-filled Magnesium

As a first example, a Mg alloy LZ21 tube was filled with barium sulfate powder and drawn via conventional cold wire drawing techniques to produce a LZ21-DFT-25%$BaSO_4$ wire (the 25% denotes 25 percent of the cross-sectional area is the powder core). Wires ranging from 0.2 to 1.0 mm were imaged via a conventional x-ray system (7). As can be seen in Figures 2 and 3, the barium sulfate core offers a substantial enhancement in wire radiopacity.

***Figure 2**. 1 mm wires of (from left): ZX10, LZ21, AZ31, and LZ21-DFT-25$BaSO_4$*

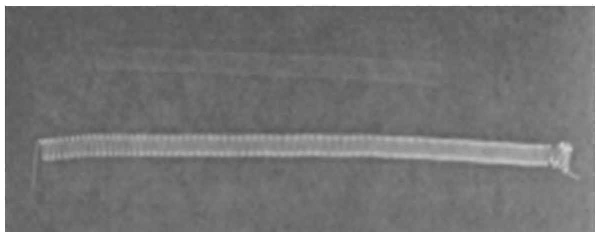

***Figure 3**. 0.2 mm LZ21 (top) and LZ21-DFT-25$BaSO_4$ (bottom) wire coiled to 1.5 mm OD.*

As a second example, Mg alloy ZX10 tubes were filled with bismuth trioxide (Bi_2O_3) and tantalum oxide (Ta_2O_5) powders and drawn to diameters as small as 0.16 mm. The resulting core percentages were approximately 30% (Figure 4, left). X-ray imaging revealed a substantial enhancement in radiopacity from Bi_2O_3, Ta_2O_5, and $BaSO_4$ over the solid Mg wire (Figure 4, right). As a practical assessment for stent visibility, a 16-end braid of 0.16 mm ZX10 wires was wrapped with a single ZX10-DFT-30Bi_2O_3 wire, significantly enhancing the radiopacity of the construct.

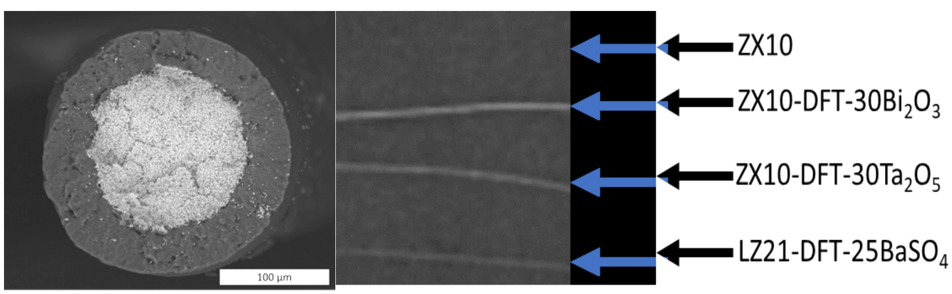

Fig. 4: Left: Tensile fracture face of a 0.25 mm ZX10-DFT®-30%Ta_2O_5 wire viewed with BSE SEM. Right: While a solid 0.2 mm Mg wire (top) is invisible under conventional x-ray conditions, wires with radiopaque powder cores are clearly visible.

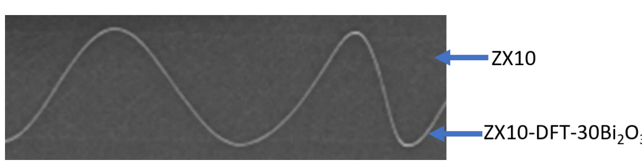

Fig. 5: An x-ray image of a 0.16 mm ZX10 wire braid wrapped with a 0.16 mm ZX10-DFT-40Bi_2O_3 wire.

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Powder-filled NiTi materials

As a third example in this series, a high strength NiTiNb alloy tube was filled with $BaSO_4$ and drawn to create a NiTiNb-DFT-60$BaSO_4$ wire. 0.25 mm wire was annealed at 400°C for 5 minutes to impart superelastic properties to the NiTiNb and the wire was cyclically tensile tested to determine upper plateau stress, lower plateau stress, ultimate stress, and permanent set. This material was compared to a NiTiNb-DFT-60Pt core as reference (Figure 7). X-ray imaging was conducted on a 16-wire braid of 0.1 mm NiTiNb-DFT-60$BaSO_4$ wire, but no enhancement in visibility was found using $BaSO_4$, indicating it is not a sufficiently radiopaque powder to enhance Nitinol's visibility.

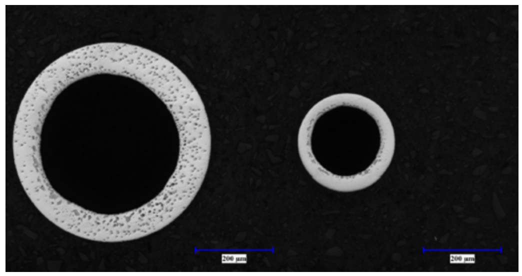

Figure 6. *Cross-sections of NiTiNb-DFT-60$BaSO_4$ wires at 0.5 and 0.25 mm diameter. The $BaSO_4$ powder was washed out during polishing. Actual core percentages measure about 50%.*

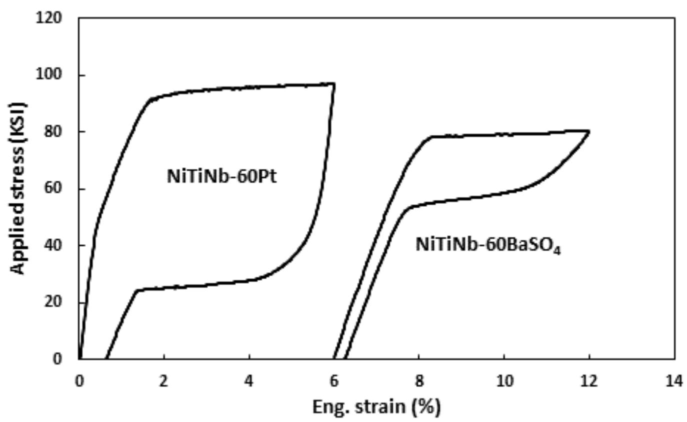

Figure 7. *The cyclic stress-strain curves from zero to six percent engineering strain of NiTiNb-DFT-60Pt (left) and NiTiNb-DFT-60$BaSO_4$ (right) at 0.25 mm show a significant increase in the lower plateau stress with the $BaSO_4$ core, and a reduction in the permanent set, in both cases due to the lack of mechanical resistance from the Pt.*

In the fourth example in this series, a NiTiNb-DFT-40WC composite wire was produced to diameters of 0.25 mm for tensile testing (Figure 8) and 0.1 mm for x-ray analysis (Figure 9). Results indicate that the tungsten carbide powder provided zero mechanical resistance to the NiTiNb and did enhance the radiopacity over standard Nitinol. NiTiNb-DFT-40WC has approximately the same radiopacity at NiTi-DFT-20Pt, and slightly less than NiTiNb-DFT-40Pt. From this, we can conclude that matching Pt-core radiopacity will require a larger powder core, whereas the powder allows for enlarging the core without the mechanical penalty. This lack of mechanical penalty could therefore allow for similar radiopacity and enhanced deployment and mechanical performance in device service.

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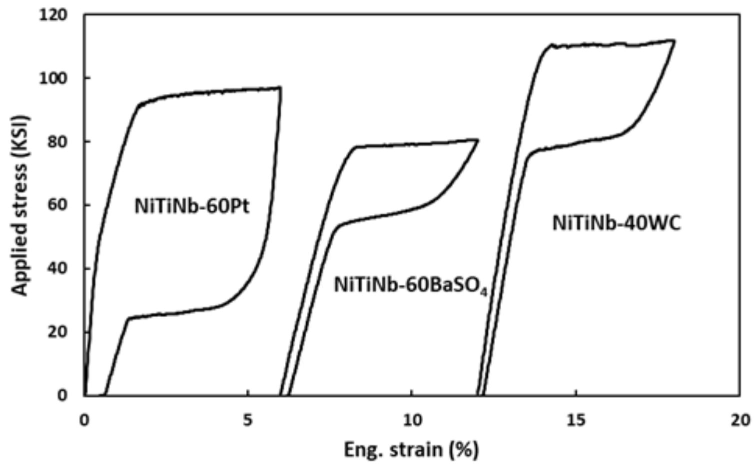

Figure 8. *The cyclic stress-strain curves from Figure 7, with the 0.25 mm wire of example 4 added on the right.*

Figure 9. *X-ray imaging of 0.1 mm wires show a 40% WC core has equivalent radiopacity to a 20% Pt core.*

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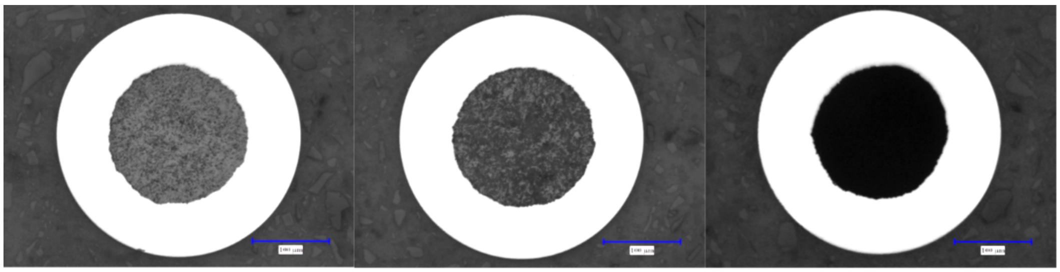
Powder-filled Cobalt Chrome materials

In a fifth example, 35N LT® tubes were filled with either Bi_2O_3, Ta_2O_5, or WC powders and drawn using conventional drawing practices to create 35NLT-DFT-40%(powder) composites with diameters of 0.320 and 0.100 mm for cross-sectional (Figure 10) and x-ray (Figure 11) analysis. For the x-ray analysis, wires were coiled around 1 mm mandrels. The three powder-core composites were compared to solid 35N LT and 35NLT-DFT-40Pt. As can be seen, all three powders offer enhanced radiopacity over the solid 35N LT. Bi_2O_3 and WC are more radiopaque than Ta_2O_5. None of the powders are as radiopaque as platinum.



35NLT-DFT-40Bi_2O_3 35NLT-DFT-40Ta_2O_5 35NLT-DFT-40WC

***Figure 10**. 0.320 mm 35N LT-DFT-powder wire cross sections. The 40% cores actually measured around 33%.*

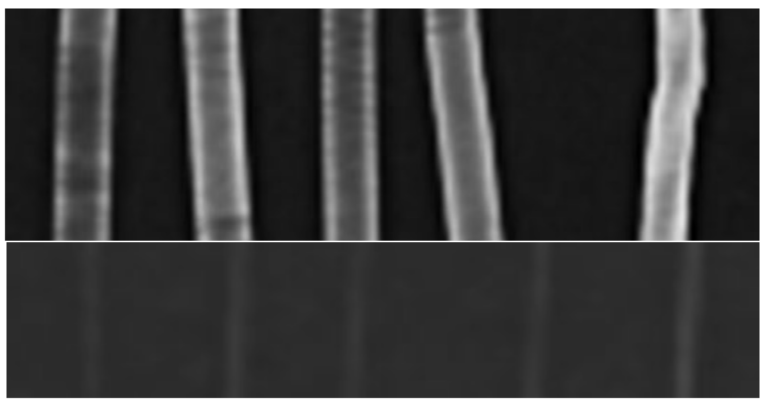


***Figure 11**. 0.1 mm wires coiled over 1 mm mandrel (top) and 0.1 mm wires (bottom).*
From left: 35N LT, 35NLT-DFT-40Bi_2O_3, 35NLT-DFT-40Ta_2O_5, 35NLT-DFT-40WC, 35NLT-DFT-40Pt.

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Biocompatibility Assessment

To gain an initial insight into relative biocompatibility of these powders, ISO 10993-5 cytotoxicity testing was conducted via the agar overlay method on Bi_2O_3, Ta_2O_5, and WC powders. Bi_2O_3 and Ta_2O_5 showed no reactivity, and WC showed mild reactivity, with all receiving a “passing” assessment. Further work to determine how these powders react in the body and where they might ultimately reside in the body is warranted. The relative concerns may also vary by device type. For example, a NiTi-DFT-Bi_2O_3 wire used in a non-degrading gastrointestinal stent may be less concerning than a Mg-DFT-Bi_2O_3 wire used in a vascular stent designed to beneficially degrade over time.

Prospective Applications Discussion

The powder-cored wires described above might find utility in a wide variety of smaller devices deployed via a transcatheter method. This could include neurovascular stents, flow diverters, and occluders, coronary stents, peripheral stents & stent grafts, valve frames, septal occluders, and venous filters. In the gastrointestinal system, devices for the upper and lower digestive tract could benefit. Enhanced radiopacity could also be useful in interventional devices such as guidewires, catheters, and stylets, to name a few.

The thin wall section could also create a more uniform stress-strain distribution across wires used in torsion, providing improved stability and durability for mechanically intensive applications.

Conclusions

A metal-sheathed, powder core, wire construct is presented with demonstration of unique and prospectively valuable device performance attributes including:

- **Improved Radiopacity:** Enhanced radiopacity is enabled in a variety of alloys including Nitinol and magnesium
- **Improved Elastic Response:** Radiopacity improvements in superelastic or shape memory Nitinol are realized without elastic mechanical property penalty
- **Improved electrochemical behavior** in more radiopaque magnesium alloy wire constructs without electromotive-driven corrosion variance during beneficial degradation.

Potential downsides of the powder-core technology include being a de facto “all new” device material, and unknown final tissue reactions in long term device outcomes.

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References

1. *Treatment planning for image-guided neuro-vascular interventions using patient-specific 3D printed phantoms.* **Russ, M., R. O'Hara, SV Setlur Nagesh, M. Mokin, Carlos Jimenez, A. Siddiqui, D. Bednarek, Stephen Rudin, and C. Ionita.** 941726, s.l. : In Medical Imaging 2015: Biomedical Applications in Molecular, Structural, and Functional Imaging, 2015, Vol. 9417.

2. *Magmaris: a new generation metallic sirolimus-eluting fully bioresorbable scaffold: present status and future perspectives.* **Claudio Rapetto, Massimo Leoncini.** Suppl 9, 2017, Journal of Thoracic Disease, Vol. 9, pp. S903-S913.

3. **Charles H. Craig, Herbert R. Radisch, Jr., Thomas A. Trozera, David M. Knapp, Timothy S. Girton, Jonathan S. Stinson.** *US20120004718A1* USA, 2002.

4. **Song Cai, Jeremy E. Schaffer, Adam J. Griebel.** *US20190292640A1* USA, 2016.

5. **Tofail, Syed A. M., et al.** *Nickel-titanium-rare earth alloy and method of processing the alloy. 8,440,031 B2* USA, 2013.

6. *Engineering characteristics of drawn filled Nitinol tube.* **Schaffer, J.E. and Gordon, R.** Asilomar, CA : In SMST-2003: Proceedings of the International Conference on Shape Memory and Superelastic Technologies (ASM International), 2004.

7. *Absorbable Wire Radiopacity: Influence of Composition and Size on X-ray Visibility.* **Adam Griebel, Aubrey Ehle, Jeremy Schaffer.** 2021, Magnesium Technology.

8. **Stinson, Jonathan.** *Bioabsorbable Marker having radiopaque constituent. US 2004/0111149A1* US, 2004.

9. *Radiopacity of experimental composite resins containing radiopaque materials.* **Aoyagi, Yujin.** 3, s.l. : Dental Materials Journal, 2005, Vol. 24.

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