An Introduction to a New Family of Palladium Based Medical Alloys

P. Hale, E. Smith, and A. Klein
Deringer-Ney Incorporated, Bloomfield, Ct., USA

Abstract

Interest has been increasing in palladium based medical alloys, as a noble metal alternative to traditional platinum based medical alloys. This work presents an overview of the palladium based alloys, Paliney In Vivo 500, 1100, and 1200. The attributes discussed are biocompatibility, mechanical properties, radiopacity, and MRI compatibility. Understanding these properties is critical in helping the device developer choose appropriate materials for a given application. For instance, the importance of understanding the response of metallic implants during magnetic resonance imaging (MRI) has increased with its ubiquitous use in the clinical setting. As a base of comparison, the properties of the Paliney In Vivo alloys are contrasted to conventional medical alloys, such as, Pt – 10.5% Ni, Pt – 10% and 20% Ir, Pt – 8% W, MP35N, Elgiloy and Inconel 625. In most cases, the appropriate Paliney In Vivo alloy has equivalent or improved performance compared to the platinum based alloys. Additionally, both the platinum and palladium based alloys are shown to have improved radiopacity and MRI imaging characteristics in comparison to both the Fe and Co based alloys. Under typical clinical conditions, a reduced magnetic susceptibility of the base alloy produced a smaller MRI ghost image. The nickel and cobalt bearing alloys have higher magnetic susceptibility and dramatically larger phantom image size.

Introduction

A palladium-rhenium alloy system has been developed, as a noble metal alternative to platinum based medical alloys. This work compares some of the pertinent properties that have made platinum and its alloys a bio-material of choice: biocompatibility, radiopacity, mechanical strength, and magnetic properties. Three, patented, palladium-rhenium alloys were developed by Deringer-Ney Inc, these are In Vivo Paliney 500, 1100, and 1200[1]. Table 1 and Table 2 list the nominal chemistry and mechanical properties of the In Vivo alloys. Biocompatibility testing, both in-vivo and in-vitro, show that the In Vivo alloys are appropriate for long term passive implantation (Table 3). Paliney 500, and Paliney 1100 offer the strength and formability comparable to platinum based alloys: Pt – 10.5%Ni, Pt – 10/20%Ir and Pt – 8%W. Paliney 1200, offers a 50% strength increase over those platinum alloys with a UTS of nearly 2000 MPa. This paper compares the MR imaging response of the new In Vivo alloys to alloys commonly used for interventional and long term implantable applications. As the clinical use of MRI continues to increase the importance of a material's MRI compatibility does as well.

The MR imaging performance may be evaluated via both direct and indirect means. The direct means, utilizes an MRI device designed for clinical use. The material is suspended in a "phantom," designed to simulate an in vivo environment. An indirect method may utilize the relationship between MR compatibility and a material's magnetic susceptibility. Magnetic susceptibility characterizes how "magnetized" a material becomes, when subjected to an external magnetic field (as in an MRI). In general, greater materials magnetic susceptibility will result in larger the displacement forces and image artifacts in the MR environment. Ferromagnetic materials have the largest magnetic susceptibilities, paramagnetic and diamagnetic materials have much lower susceptibilities. Because of the strong interaction of ferromagnetic materials with an external field, the resulting physical force on them tends to preclude their use in an MR environment.

Numerous studies have been done to address the interaction of materials and devices with MRI techniques. A few of these include the general material relationship between magnetic susceptibility and MRI response[2]; the general MRI compatibility of devices[3,4,5,6,7,8]; physically induced forces during MRI[4,6,9]; MRI induced heating[4,6,10,11]; and MR image artifacts[4,12,13,14,15,16]. Additionally, the regulatory community has been involved, to ensure patient safety[17, 18] and provide evaluation standards[19, 20, 21, 22].

Experimental Procedure

The magnetic susceptibility, MR image, and x-ray image were compared for platinum group metal (PGM), and non-PGM based medical implant materials. Table 2 lists the materials tested and nominal mechanical properties. Table 1 and Table 4 list the nominal chemistries.

Volumetric magnetic susceptibility (cgs units) was measured using a Johnson Matthey, MSB-Auto, balance. Sample rods were either 0.160" or 0.120" diameter, and a minimum of 2" long. The MSB-Auto, automatically detects which of the two standard sample diameters are used, to calculate the sample volume. To confirm measurement validity, samples were made from Pt, Pd, and Ag, and compared to literature values (Table 5).

X – Ray radiographs were taken of tight wrapped coils with an outer diameter of 0.66 mm (.026”, Figure 1). The radiographic instrument was an Associated X – Ray Corporation Minishot. The accelerating potential was set at 80 keV.

Magnetic resonance imaging was done, for each alloy, on wire, 0.003” (0.076mm) in diameter. Two sample configurations were tested, straight wire, and tight wrapped coils with an outer diameter of 0.026” (0.66 mm, Figure 1). All sample lengths were approximately 1” (2.54 cm). The coils were imaged in two orientations, coil axis parallel and perpendicular to the primary magnetic field (Figure 2).

Magnetic resonance imaging experiments and calculations were done at Yale University’s Magnetic Resonance Research Center. The MR instrument was a 3.0 Tesla Siemens Trio. Each sample was imaged, in a gelatin phantom, both parallel and perpendicular to the primary magnetic field, B_0. The imaging parameters were: 190 x 190 mm^2 field of view, 4 mm slice thickness, 260 hz/pixel bandwidth, 256 x 256 pixel matrix, TR/TE ratio of 900/2.77 ms and 90^0 flip angle. The temperature rise during imaging was estimated using the proton resonance frequency method[23].

Results

For each alloy tested, Table 6 shows the magnetic susceptibility, MR images, and radiographs. As the magnetic susceptibility decreases, the distortion of the MR image decreases. Images taken with the coil axis parallel to B_0 show larger, but more uniform distortion than those taken normal to B_0. The data show that the In Vivo family of palladium alloys (Paliney 500, 1100, and 1200) has comparable magnetic and radiographic properties to Pt-8W, Pt-10Ir, and Pt-20Ir. Of the PGM alloys, the Pt-10.5Ni has the largest MR image distortion and the largest magnetic susceptibility. The non- PGM alloys exhibit the highest susceptibilities, have the largest MR image distortion, and are much less radiopaque than the PGM alloys.

The estimated temperature rise of the samples during MR testing is listed in Table 7. The maximum temperature rise for the: Pd alloys was 0.2^{o}C, Pt alloys was 0.35^{o}C, and non-PGM alloys was 0.4^{o}C.

Discussion

For the evaluation of MRI compatibility, three primary material responses to MR are measured: magnetically induced force, MR image distortion, and device heating. The degree of induced force and image distortion may be inferred from measurement of the magnetic susceptibility. The palladium alloys examined show medical imaging performance characteristics as good as the best, common, commercial alloys.

The data reinforces the trend, established in the literature, that MR image distortion increases with increasing magnetic susceptibility[14]. The PGM alloys provide a design advantage over Ni, Co, and Fe based alloys, because they can offer both MRI compatibility, and radiopacity. Thus the use of a precious metal implant may then provide enhanced functionality. Additionally, palladium based alloys have a much lower raw material cost than platinum alloys, with similar performance.

During imaging no sample movement was observed. Under test parameters, such as those used by Kangarlu and Shellock[9], no sample movement would be anticipated for an In Vivo alloy, given their low magnetic susceptibilities.

No gross heating was observed, associated with the RF field, as a result of the gradient echo imaging sequence. Sample heating has been the topic of many research efforts, and for metallic implants, is highly geometry dependent[4, 6, 10, 21]. The intent of these observations was to determine if any gross heating effects could be seen. To fully characterize any occurance of heating, a more detailed study would be necessary.

Conclusions:

1. Paliney 500 alloy offers a suitable, lower cost, replacement for Pt-Ir alloys containing less than 10 % Ir.
2. Paliney 1100 alloy offers a suitable, lower cost, replacement for Pt – 10.5%Ni, Pt – 20%Ir and Pt – 8%W alloys.
3. Paliney 1200 offers both improved radiopacity and MR visibility as compared to cobalt and nickel based superalloys, with equivalent strength.
4. In general, the MRI artifact size decreases with decreasing magnetic susceptibility.
5. Image artifacts were less uniform when the coils were oriented parallel to the primary magnetic field.
6. Image artifacts were more uniform, but larger and more pronounced when the coils were oriented perpendicular to the primary magnetic field.

References

1. Klein, A. and Smith, E., “Palladium Alloy,” US Patent 7354488, April 8, 2008
2. Schenck, J. “The role of magnetic susceptibility in magnetic resonance imaging: MRI magnetic

compatibility of the first and second kinds" Med. Phys. 23 (6), June 1996

3. Shellock, F. and Crues, J. "MR Procedures: Biologic Effects, Safety, and Patient Care." Rad, 232 (3), September 2004
4. Schueler, B. "MRI Compatibility and Visibility Assessment of Implantable Medical Devices." J Mag Res Im, 9, 596-603, 1999
5. Martin, E. et al. "Magnetic resonance imaging and cardiac pacemaker safety at 1.5-Tesla." J Am Col Card, 43 (7), 2004
6. Nyenhuis, J. et al. "MRI and Implanted Medical Devices: Basic Interactions With an Emphasis on Heating." IEEE Tans on Dev and Mat Rel, 5 (3) September 2005
7. Numaguchi, Y. et al. "Platinum coil treatment of complex aneurysms of the vertebrobasilar circulation." Neuroradiology, 34, 252-255, 1992
8. Hennemeyer, C. et al. "In Vitro Evaluation of Platinum Guglielmi Detachable Coils at 3 T with a Porcine Model: Safety Issues and Artifacts." Radioloty, 219 (3), June 2001
9. Kangarlu, A. and Shellock, F. "Aneurysm Clips: Evaluation of Magnetic Field Interactions With an 8.0 T MR System." J Mag Res Im, 12, 107-111, 2000
10. Mattei, E. et al. "Complexity of MRI induced heating on metallic leads: Experimental measurements of 374 configurations." BioMed Eng. OnLine, 7(11), 2008
11. Busch, M. et al. "Finite volume analysis of temperature effects induced by active MRI implants with cylindrical symmetry: 1. Properly working devices." BiMed Eng OnLine, 7 (11), 2008
12. Beuf, O. et al. "Correlation between magnetic resonance imaging disturbances and the magnetic susceptibility of dental materials." Dent Mater, 10:265-268, July, 1994
13. Zwarun, A. "Relationship of magnetic moment of metallic alloys to image artifact during magnetic resonance imaging" Med Lasers and Sys, Vol 1650, 1992
14. Matsuura, H. et al. "Quantitative Analysis of Magnetic Resonance Imaging Susceptiblity Artifacts Caused by Neurosurgical Biomaterials: Comparison of 0.5, 1.5, and 3.0 Tesla Magnetic Fields." Nerol Med Chir (Tokyo), 45, 395-399, 2005
15. Shafiei, F. et al. "Artifacts from Dental Casting Alloys in Magnetic Resonance Imaging." J Dent Res, 82 (8), 602-606, 2003
16. Honda, M. et al. "Artifacts from Dental Casting Alloys in Magnetic Resonance Imaging." Mag Res in Med Sci, 2 (2), 71-77, 2003
17. FDA, CDRH Magnetic Resonance Working Group. "A Primer on Medical Device Interactions with Magnetic Resonance Imaging Systems." February 7, 1997
18. FDA, Guidance for Industry and FDA Staff. "Establishing Safety and Compatibility of Passive Implants in the Magnetic Resonance (MR) Environment." Doc 1685, August 21, 2008
19. ASTM F2052, "Standard Test Method for Measurement of Magnetically Induced Displacement Force on Medical Devices in the Magnetic Resonance Environment."
20. ASTM F2213, "Standard Test Method for Measurement of Magnetically Induced Torque on Medical Devices in the Magnetic Resonance Environment"
21. ASTM F2182, "Standard Test Method for Measurement of Radio Frequency Induced Heating Near Passive Implants During Magnetic Resonance Imaging"
22. ASTM F2119, "Standard Test Method for Evaluation of MR Image Artifacts from Passive Implants"
23. Constable, R. T., personal communication, Yale University, New Haven, CT
24. CRC Handbook of Chemistry and Physics, 83rd Ed., "Magnetic Susceptibility of the Elements and Inorganic Compounds" CRC Press, 2002
25. HPMetals, "MP35N-LTi Data Sheet." Rev 0 March 14, 2003

Acknowledgements

The authors would like to thank Professor Todd Constable of the Yale University School of Medicine for conducting the MRI experiments. They would also like to thank Jeff Gallmeyer and Dave Plumley of Fort Wayne Metals for providing wire samples and Plamen Jedamanov of Deringer Ney for assistance in sample preparation. Jessie Burke of Cook Inc. took the radiographs.

Table 1: Nominal Chemical Analysis of Platinum Group Alloy Wires. Compositions are in weight percent.

Alloy	*Pd*	*Re*	*B*	*Pt*	*Ni*	*W*	*Ir*
Paliney 500	*94.9*	*5*	*0.1*				
Paliney 1100	*89.9*	*10*	*0.1*				
Paliney 1200	*87.8*	*12*	*0.2*				
Pt – 10.5%Ni				*89.5*	*10.5*		
Pt – 8%W				*92*		*8*	
Pt – 10%Ir				*90*			*10*
Pt – 20%Ir				*80*			*20*

Table 2: Metallurgical state, ultimate tensile strength, and tensile elongation to failure, for implant alloys.

Alloy	*State*	*UTS(MPa)*	*%Elong*.
Paliney 500	*S.R.*	*750*	*4*
Paliney 1100	*S.R.*	*1,300*	*4*
Paliney 1200	*S.R.*	*1,925*	*1.5*
Pt – 10.5%Ni	*S.R.*	*1,200*	*5*
Pt – 8%W	*S.R.*	*1,300*	*6*
Pt – 10%Ir	*S.R*	*750*	*2*
Pt – 20%Ir	*S.R.*	*1250*	*2*
MP35N	*Hard*	*1,900*	*10*
Elgiloy	*Hard*	*1,875*	*2.5*
Inconel 625	*Hard*	*1,925*	*3*

S.R = Stress Relieved, Hard = as – drawn

Table 3: Biocompatibility test results for In Vivo alloys: Paliney 500, 1100, and 1200. Note, * tests performed on Paliney 1100 only.

Test	Result
1) Cytotoxicity – ISO 10993-5 ISO Elution Method	No evidence of toxic reaction
2) Intracutaneous* – ISO 10993-10 aqueous and organic extraction	No evidence of irritation
3) Systemic Toxicity – ISO 10993-11 aqueous and organic extraction	No evidence of toxicity
4) Muscle Implant – ISO 10993-6 2* week, 12 week, and 26* week	Implant material classified as nonirritant
5) InVitro Hemolysis* – ISO 10993-4 aqueous extraction (modified ASTM)	Alloy considered nonhemolytic

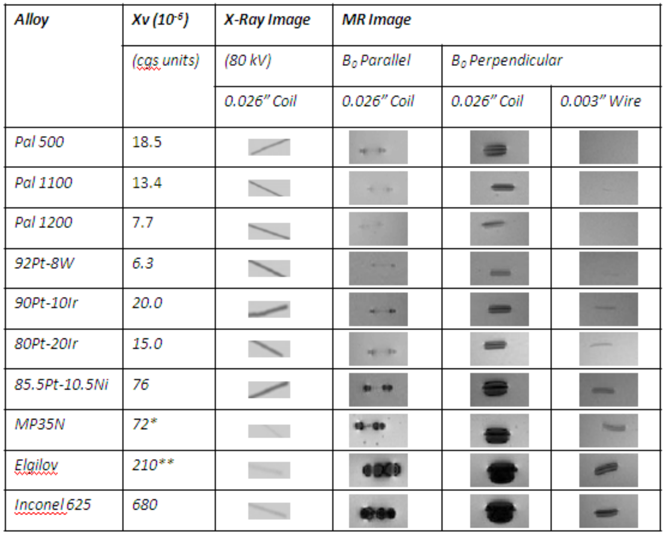
Table 4: Nominal Chemical Analysis of non Platinum Group Alloys. Compositions are in weight percent.

Alloy	*Ni*	*Co*	*Cr*	*Mo*	*Fe*	*Mn*	*Nb+Ta*	*Ti*	*C*
MP35N	*35*	*35*	*20*	*10*					
Elgiloy	*15*	*40*	*20*	*7*	*16*	*2*			
Inconel 625	*53.35*		*21.5*	*9*	*2.5*		*3.65*		

Table 5: Measured volumetric magnetic susceptibility (cgs) of pure metals, compared to literature values[24].

Metal	*Xv (This Study)*	*Xv (Literature Value)*
Pd	*7.500E-05*	*6.099E-05*
Pt	*2.700E-05*	*2.100E-05*
Ag	*-1.810E-06*	*-1.898E-06*

Table 6: Magnetic susceptibility (cgs) of implant alloys, with x-ray and MR images.



Alloy	*Xv* (10^{-6})	*X-Ray Image*	*MR Image*		
	(cgs units)	*(80 kV)*	*B_0 Parallel*	*B_0 Perpendicular*	
		0.026" Coil	*0.026" Coil*	*0.026" Coil*	*0.003" Wire*
Pal 500	18.5				
Pal 1100	13.4				
Pal 1200	7.7				
92Pt-8W	*6.3*				
90Pt-10Ir	*20.0*				
80Pt-20Ir	*15.0*				
85.5Pt-10.5Ni	*76*				
MP35N	*72**				
Elgiloy	*210***				
Inconel 625	*680*				

*Ref 25, calculated from magnetic permeability
** Ref 14

Table 7: Artifact size, angular deflection and temperature rise of 0.026" in diameter simple coils in parallel and perpendicular orientations to the magnetic field.

Alloy	***Temperature rise (^{0}C)***	
	Parallel to B_0	*Perpendicular to B_0*
Paliney 500	*0.1*	*0.2*
Paliney 1100	*0.1*	*0.2*
Paliney 1200	*0.1*	*0.1*
Pt – 10.5%Ni	*0.35*	*0.2*
Pt – 8%W	*0.1*	*0.2*
Pt – 10%Ir	*0.1*	*0.2*
Pt – 20%Ir	*0.15*	*0.1*
Elgiloy	*0.4*	*0.4*
MP35N	*0.4*	*0.3*
Inconel 625	*0.4*	*0.4*

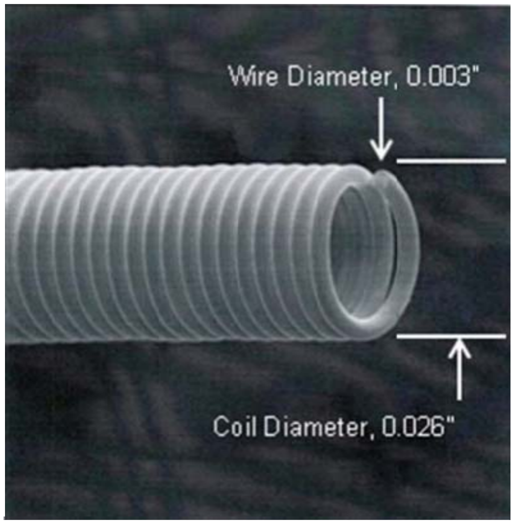


Figure 1: Scanning electron image of a coil of Paliney 1100 used for this work. Coil diameter and wire diameter are labeled. Coils were 1" long.

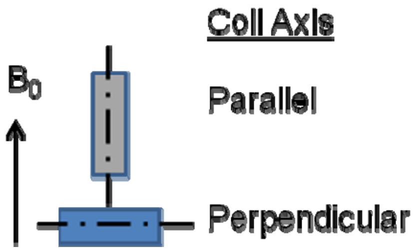


Figure 2: Schematic showing the two sample orientations used, relative to the primary magnetic field (B_0)