Developing Radiopure Copper Alloys for High Strength Low Background Applications

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Electroformed Copper is used for near-detector parts

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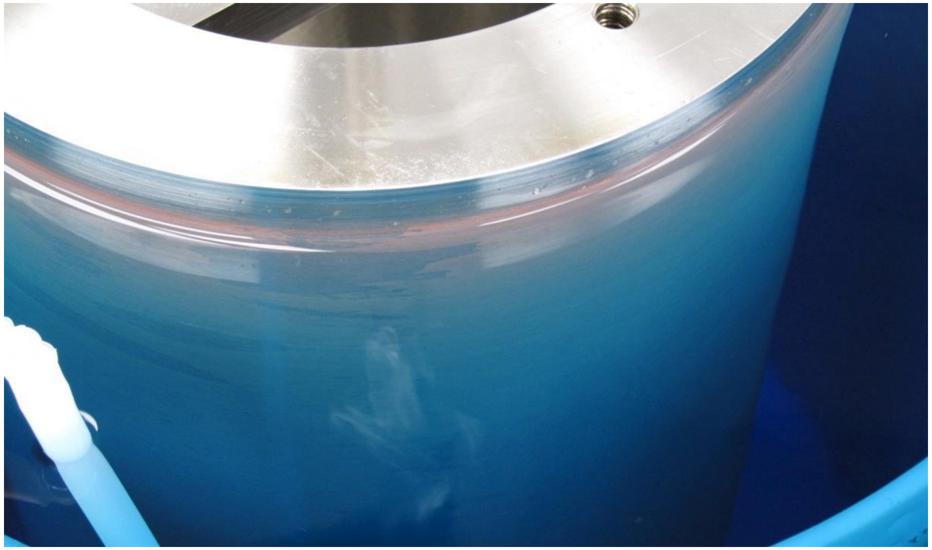
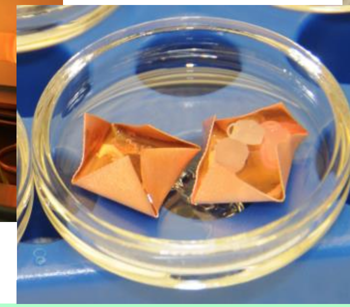


Cu parts for ββ(0ν) experiment, The Majorana Demonstrator, are purified and produced through Electroforming at both PNNL and SURF

(previous talk by Christofferson)

Assay Capability

Previous talk by Arnquist



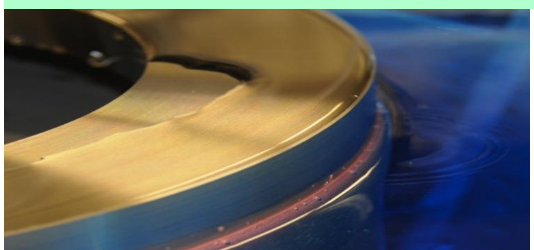
Proven sample preparation knowledge and chemistry experience to assay most any matrix

Two dedicated ICP-MS instruments for physics assay for ultra low ^{40}K, ^{232}Th, ^{238}U, etc.
CASCADES 14-Crystal HPGe Spectrometer, variety of others

Class 1000-10,000 cleanroom labs (with Class 10-100 laminar flowhoods) and Shallow Underground Laboratory dedicated to ULB materials and assay

Materials Capability

Proven knowledge, experience, and facilities to electroform and assay the most radiopure copper in the world



	Th-232		U-238	
	fg/g Cu	µBq/kg Cu	fg/g Cu	µBq/kg Cu
Method Detection Limit¥	8.4	0.034	10.6	0.131

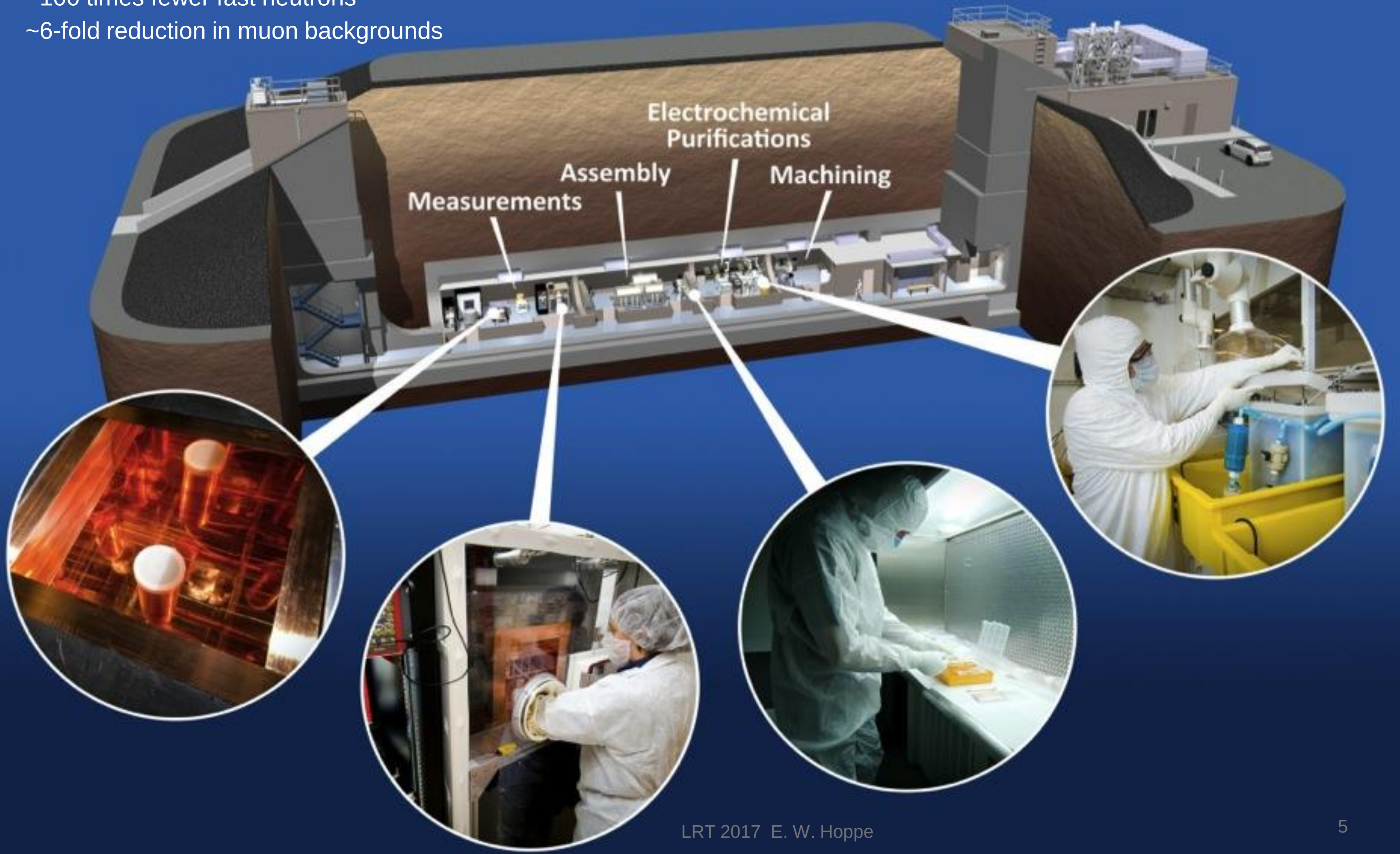
Advanced facilities and staff to machine, etch, clean, package, and handle various ultralow background (ULB) materials.

¥ Nuclear Instruments and Methods in Physics Research A 775 (2015) 93-98.

Underground lab provides low backgrounds for measurements and materials synthesis

Effective depth: ~37 mwe

- ~100 times fewer fast neutrons
- ~6-fold reduction in muon backgrounds



Physical Properties of Electroformed Copper

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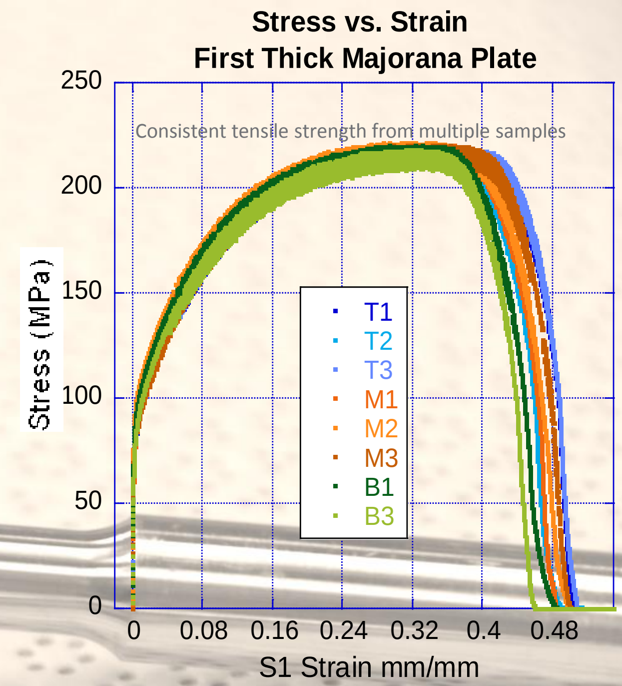
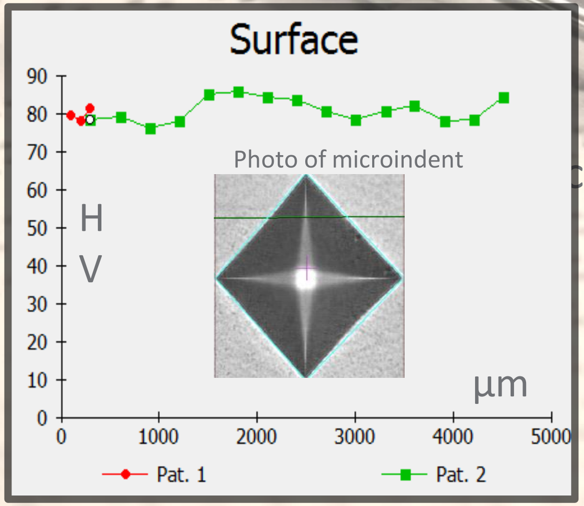
Electroformed copper is evaluated for grain size, hardness, and tensile strength
(most commercial OFHC copper is <10 ksi)



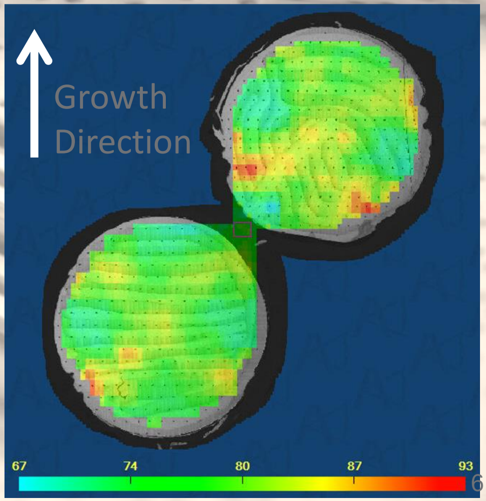
Yield Strength: 13.78 ± 0.58 ksi
Ultimate Tensile Strength: 31.2 ± 0.73 ksi
Young's Modulus: 9.34E3 ± 1.74E3 ksi

- Significant Strain hardening
- Significant Ductility



Hardness measured across a surface

Electroformed copper shows consistency in mechanical response from tensile and hardness testing on different regions across the material profile



Hardness contour map across a surface

Challenges with Copper

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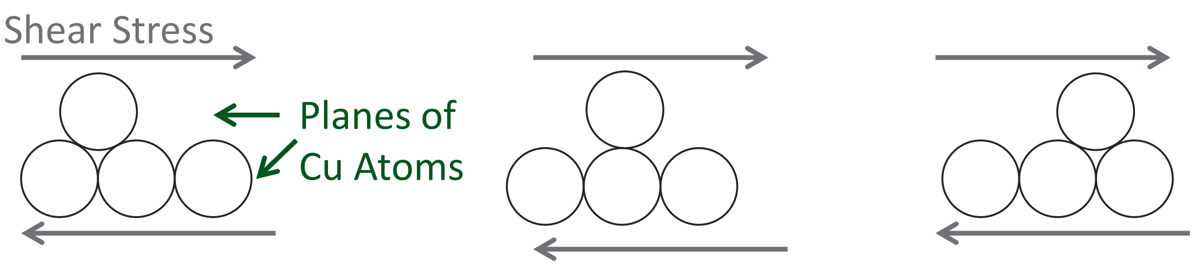
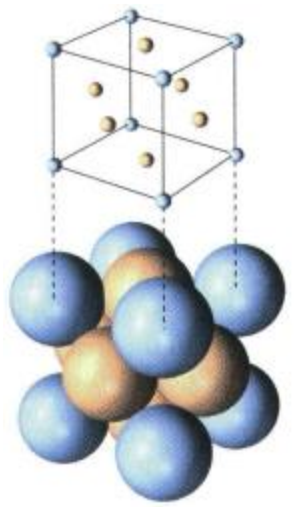
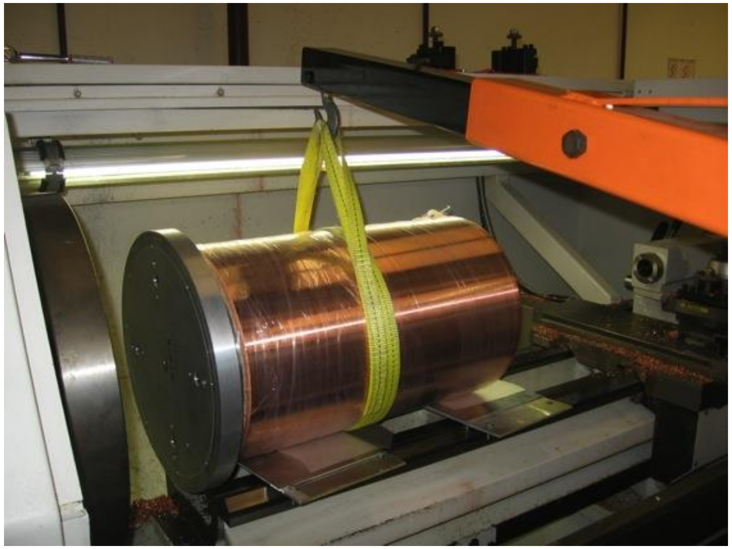
- High ductility from FCC structure





- Difficult to machine
- Threaded parts deform & gall
- Increased strength would reduce the mass of non-detector material
- Strength limits applications
  - Bolts, Pressure vessels

(for example see talk by Fard, NEWS-G)



Copper Alternative

A higher strength radiopure material is needed

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.008																	2 **He** 4.0026
3 **Li** 6.94	4 **Be** 9.0122											5 **B** 10.81	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.180
11 **Na** 22.990	12 **Mg** 24.305											13 **Al** 26.982	14 **Si** 28.085	15 **P** 30.974	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.948
19 **K** 39.098	20 **Ca** 40.078	21 **Sc** 44.956	22 **Ti** 47.867	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.845	27 **Co** 58.933	28 **Ni** 58.693	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.723	32 **Ge** 72.630	33 **As** 74.922	34 **Se** 78.97	35 **Br** 79.904	36 **Kr** 83.798
37 **Rb** 85.468	38 **Sr** 87.62	39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.95	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57-71 *	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89-103 #	104 **Rf** (265)	105 **Db** (268)	106 **Sg** (271)	107 **Bh** (270)	108 **Hs** (277)	109 **Mt** (276)	110 **Ds** (281)	111 **Rg** (280)	112 **Cn** (285)	113 **Nh** (286)	114 **Fl** (289)	115 **Mc** (289)	116 **Lv** (293)	117 **Ts** (294)	118 **Og** (294)

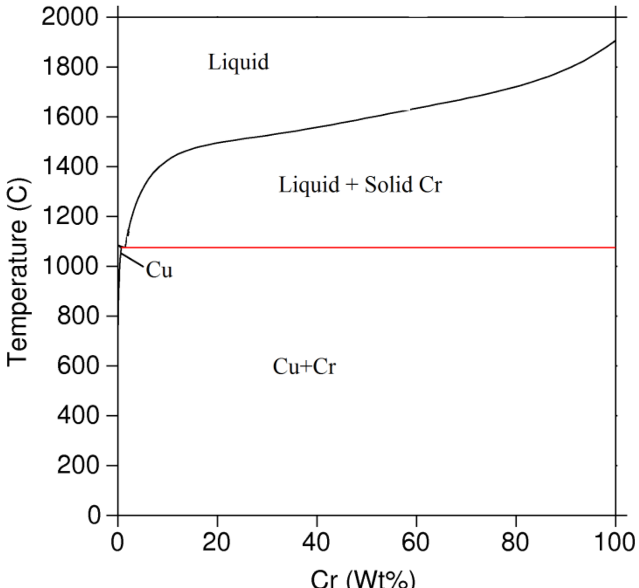
* Lanthanide series	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.05	71 **Lu** 174.97
# Actinide series	89 **Ac** (227)	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

1. Radiopure – no natural radioisotope
2. Improved strength compared to copper
3. Higher resistance to plastic deformation
4. Fiscally viable

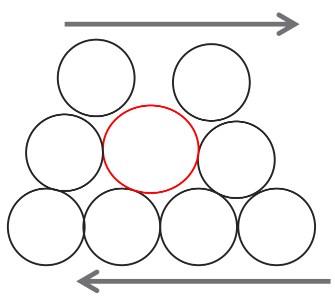
Copper Alternative

Metal/Alloy	Yield Strength (Mpa)	Ultimate Strength (Mpa)
Commercial Cu	70	220
Electroformed Cu	90	250
Cu/Cr alloys	120	420
Al	30	90
Ti	100	300
Steel	200	1700

Highly generalized strength data



Cu-Cr is a precipitation hardened alloy

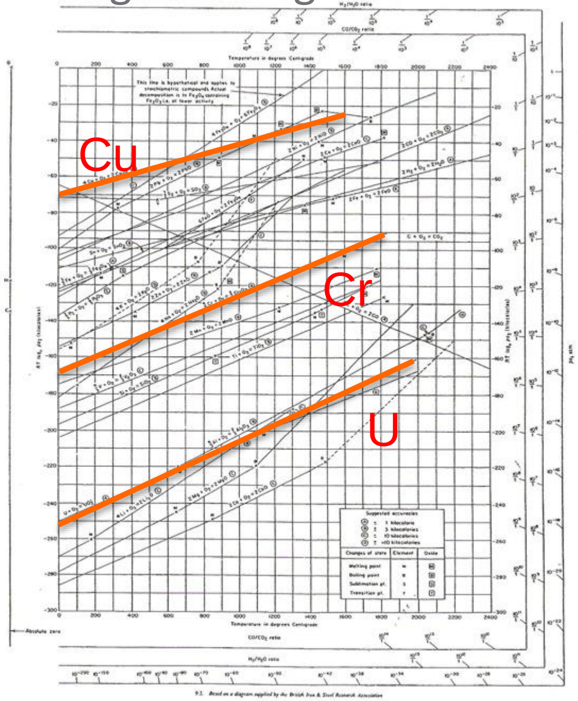


Introduction of Cr to copper lattice increases strain (strength) and creates slip plane interruption (pinning)

Cu-Cr Alloy

U and Th can be excluded from Cr through electrolysis just as is done with Cu

Ellingham Diagram



Standard half-cell potentials

Metal	Reaction	E° (V)	ΔE°$_{Th}$(V)	ΔE°$_{U}$(V)
Cu	$Cu^{2+} + 2e^- \leftrightarrow Cu_{(S)}$	0.34	-2.17	-1.98
Cr	$Cr^{3+} + e^- \leftrightarrow Cr^{2+}$	-0.42	-1.41	-1.22
	$Cr^{2+} + 2e^- \leftrightarrow Cr_{(S)}$	-0.89	-0.94	-0.75
	$Cr^{3+} + 3e^- \leftrightarrow Cr_{(S)}$	-0.74	-1.09	-0.9
	$0.5Cr_2O_7{}^{2-} + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 3.5H_2O$	1.10	-2.93	-2.74
U	$U^{3+} + 3e^- \leftrightarrow U_{(S)}$	-1.64	-0.19	0
Th	$Th^{4+} + 4e^- \leftrightarrow Th_{(S)}$	-1.83	0	0.19

$$E = E^0 + \left(\frac{RT}{zF}\right) \ln \left\{\frac{\prod a_{react}}{\prod a_{prod}}\right\}$$

- Cr is much more active than Cu, but still far above U and Th
- The reduction potentials of Cu and Cr may be too far apart to co-deposit from a single electrolytic cell

Ultra-Radiopure Alloys Development

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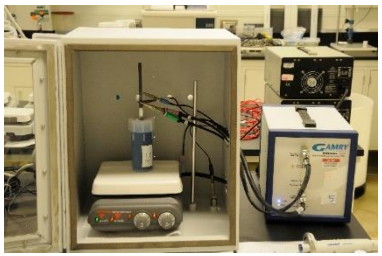
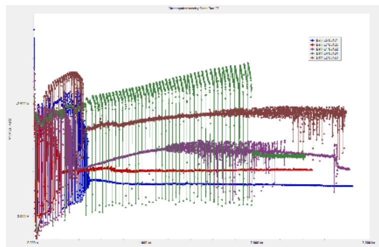
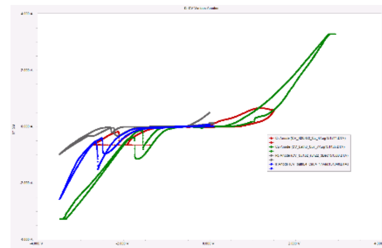
- Electrochemical Investigations
  - Determining suitable electrolyte composition & conditions, electrode material response, deposition potential, kinetics, etc… **Many** tests by Anne-Marie Suriano



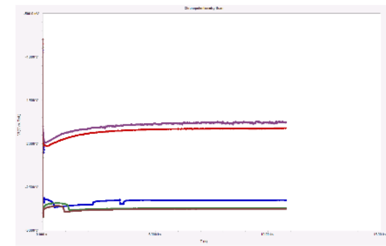
Potentiostatic Studies



Effect of Cathode Morphology

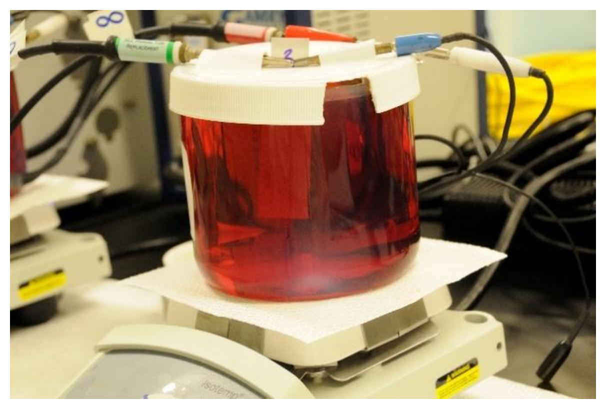


Anode Performance

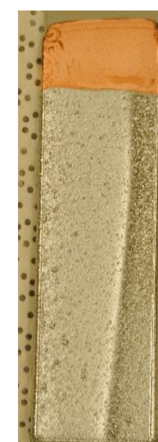


Effect of Electrode Size

- Materials Purification
  - Growing crystalline metallics electrolytically to exclude radioactive contaminants



Cleanroom Lab plating set-up for duel-bath method



Cr on Cu

Electroplated Cu-Cr Alloy

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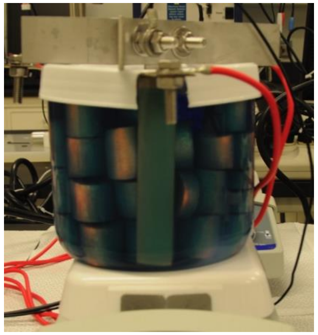
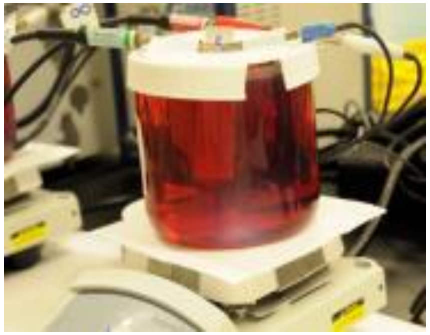
Cu and Cr are electrorefined in separate cells



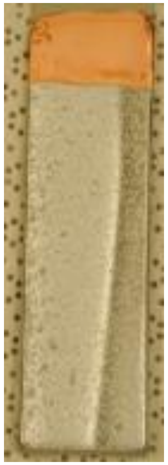
Cu Cell

+

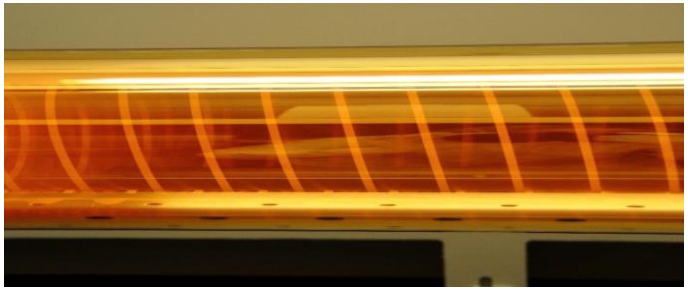


Cr Cell

=



Then heat treated to alloy



Tube Furnace

Cr diffused in Cu

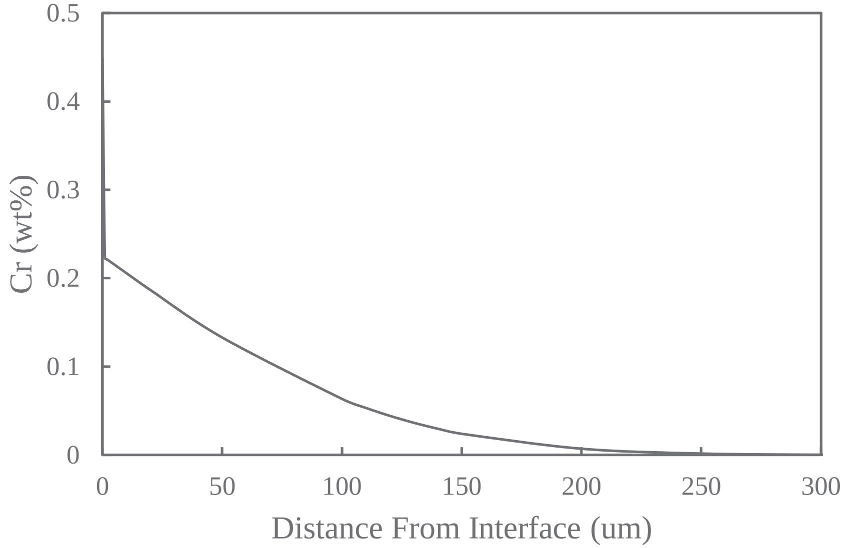
Alloying

The first step of alloying layered electrorefined Cu and Cr is *Solution Treating*

The Cr layer is diffused into the Cu layer

- The diffusion coefficient states the distance Cr can diffuse
- The phase diagram states the Cr solubility in Cu

The solid solution is quenched, trapping Cr in solution



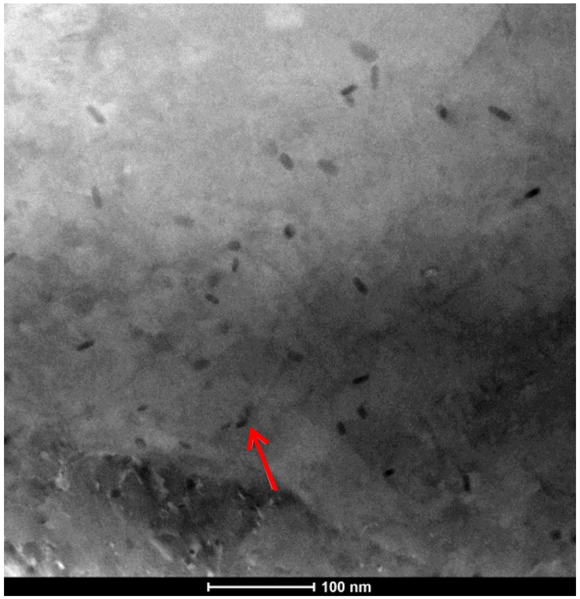
Literature Cr Diffusion coefficient at 1000 °C 24 hrs

- Literature diffusion coefficient: 5.086×10^{-10} cm²/s
- Observed Cr Diffusion coefficient: 8.9×10^{-9} cm²/s

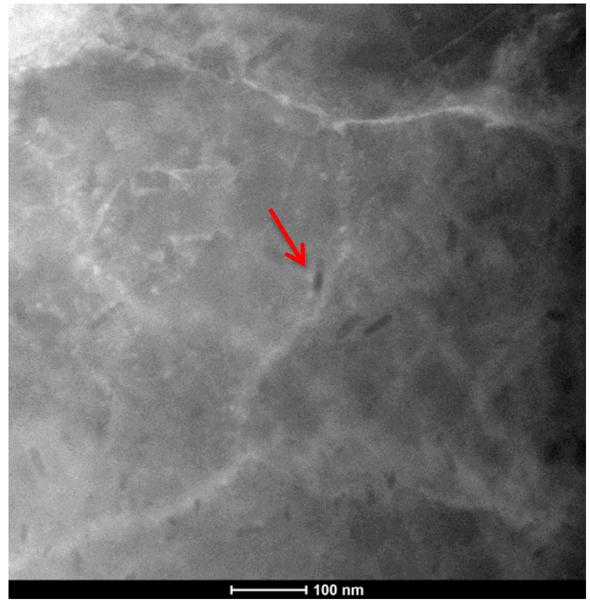
.

Heat Treatments

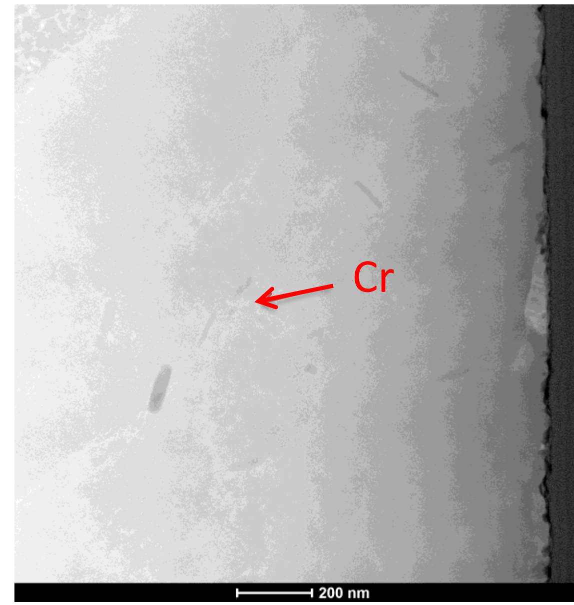
500 °C 12hrs



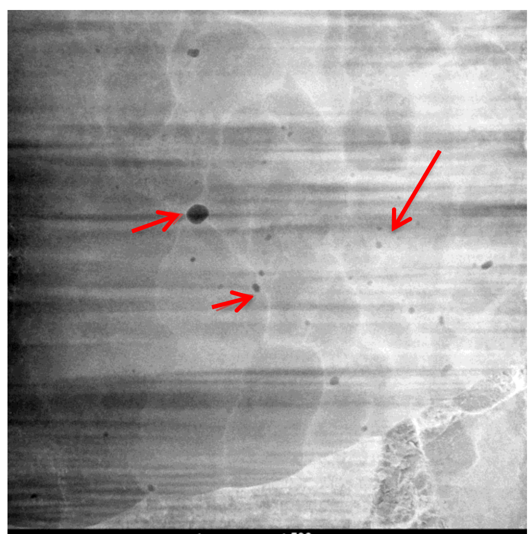
600 °C 4hrs



600 °C 12hrs



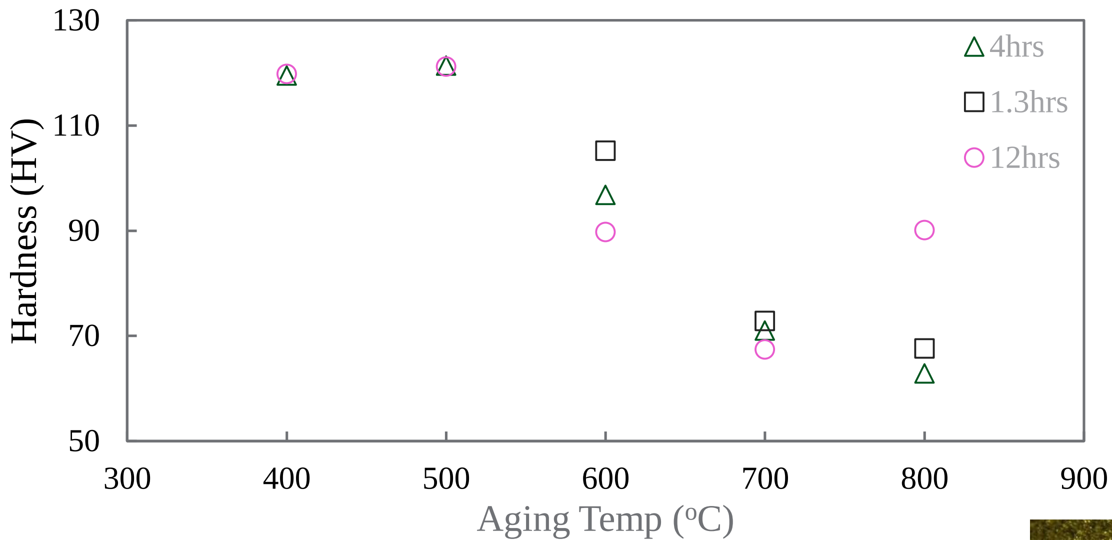
(TEM images taken at EMSL facility, PNNL)



600 °C 4hrs
Intermediate cold working

Hardness

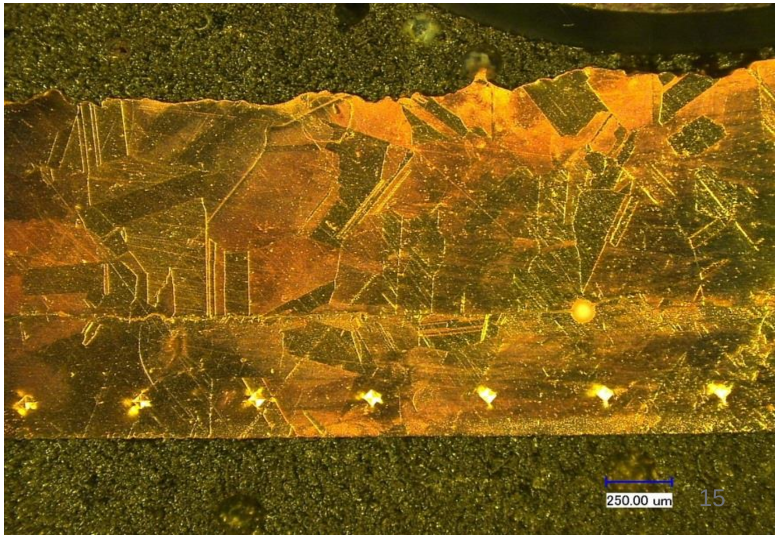
Aging Curves show the change in hardness as Cr precipitates form



Heat Treated Cu-Cr

Maximum hardness at 500 °C 12 hrs

Showing hardness indents



Hardness

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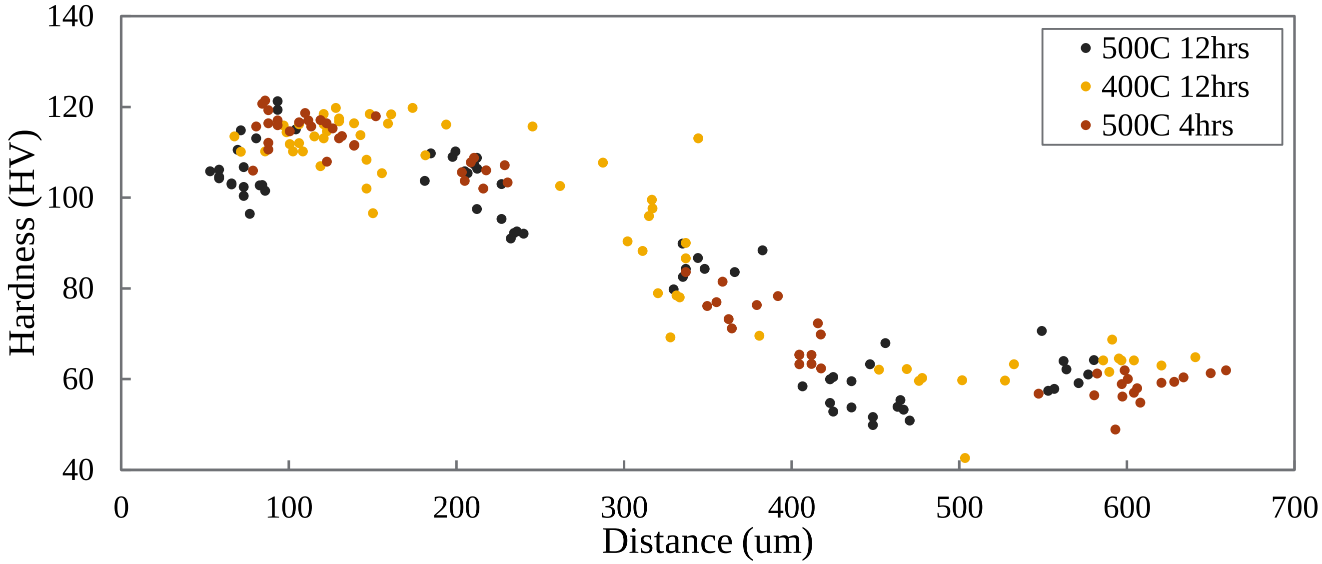
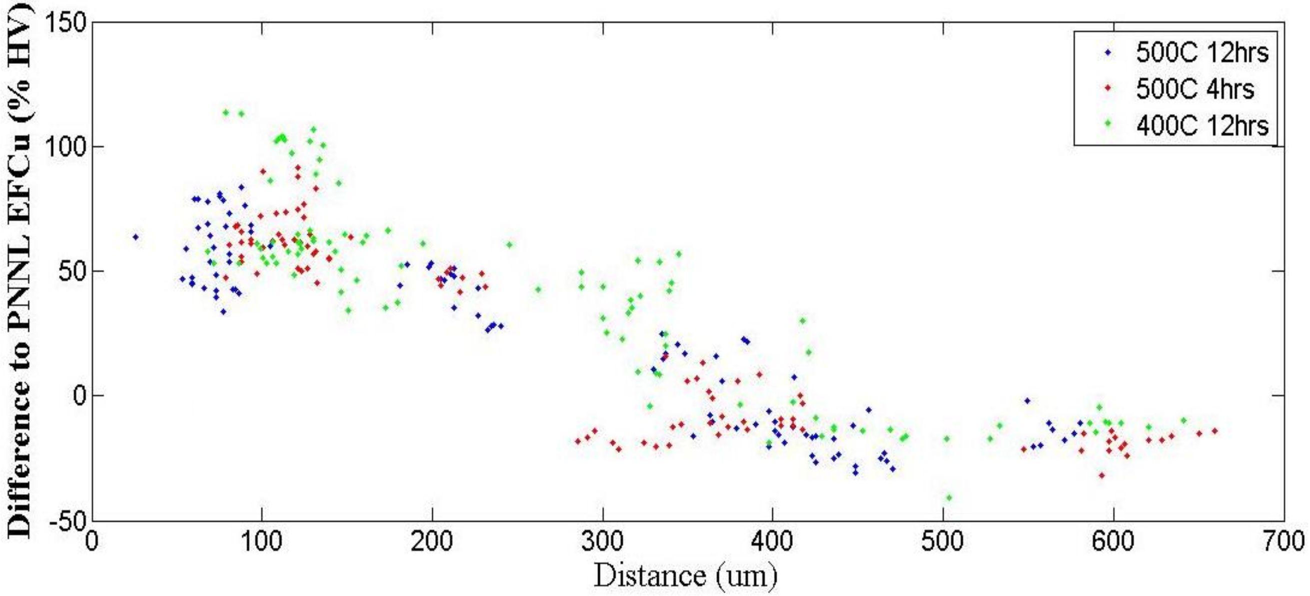
Hardness from original Cu-Cr interface

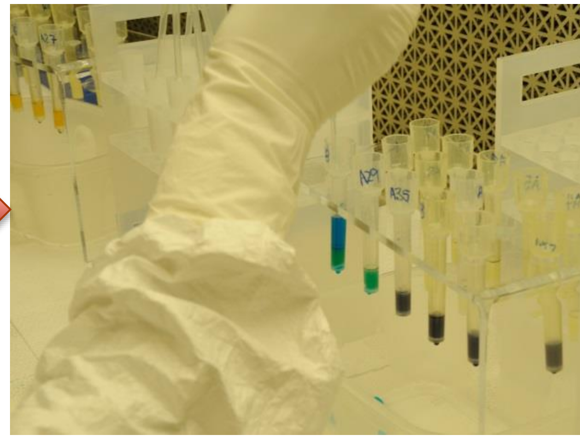


Hardness increase over EFCu



Cu/Cr Purity

Radiopurity is determined by ICP-MS assay of uranium and thorium



Electroplated Cr radiopurity

Sample	C_{Th} (pg_{Th}/g_{Sample})	+/- sd	C_U (pg_U/g_{Sample})	+/- sd
Cr	8.72	0.32	2.37	0.61
EFCu	0.011	0.005	0.017	0.003
Cu-Cr Alloy*	0.062	0.007	0.031	0.007

* Predicted value based on 0.585 wt% Cu-Cr alloy

Rejection rate

Sample	Rejection rate	
	Th	U
Cr	20.82	94.76
EFCu	855	862

Journal of Radioanalytical and Nuclear Chemistry, Vol. 277, No.1 (2008) 103–110

Conclusions

A radiopure Cu-Cr alloying process has been developed

- Peak hardness:121.39 HV vs. EFCu 72 HV
  - Higher strength can be achieved with higher Cr content but limited by overall diffusion/solubility
- Predicted Radiopurity: 0.062 pg_{Th}/g_{Cr} and 0.031 pg_{U}/g_{Cr}
  - Improved radiopurity can be achieved with higher purity starting Cr and components

With a 1000 ^{o}C 24 hr solution treatment:

- Observed Cr Diffusion coefficient: 8.9×10^{-9} cm^2/s, faster and further than literature diffusion coefficient: 5.086×10^{-10} cm^2/s
  - Perhaps crystal structure of underlying electroformed copper encourages diffusion?
- Peak aging: 500 ^{o}C 12 hrs
- Cr content: 0.585 Wt %

Future Work

- Complete tests of alloy at additional Cr content
- Demonstrate scale up by producing larger samples/parts, conduct mechanical properties testing
- Conduct radiopurity assays (U, Th, K, etc.) of material produced at larger scale
- Perform physical properties tests (thermal and electrical conductivity, emissivity)

Thank you