Characterization of Additively Manufactured GRCop-42 And GRCop-84

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The Application - Regeneratively Cooled Rocket Engine Main Combustion Chamber Liners

- **Rocket engine liners have complex internal cooling channels (flowing propellants) required to keep the liners from melting**
- **A major shift has occurred in their manufacturing**
  - The traditional subtractive and joining methods were costly and required months or even years to make a chamber assembly
  - Additive manufacturing decreases cost and time significantly while enabling new designs
- **Changing to Laser Powder Bed Fusion (L-PBF) additive manufacturing requires detailed characterization to confirm that the new method will produce similar thermophysical and mechanical properties compared to traditional manufacturing methods**

30,000 lb_f class GRCop-84 combustion chamber liner made from L-PBF

Hot Fire Test Of 30k lb$_f$ AM LPBF GRCop-84 Engine Liner (Low Cost Upper Stage Program)

Full video at:
https://www.youtube.com/watch?v=FfeP4BVTsps&ab_channel=NASA%27sMarshallSpaceFlightCenter

Material Requirements for GRCop Alloys

- **Liner material must have**
  - High thermal conductivity
  - Higher elevated temperature strength up to 700-800 °C
  - Longer low cycle fatigue (LCF) life
  - Longer creep life / slow creep rate
- **In addition, low thermal expansion is desired to help minimize thermally induced stresses**

- **GRCop Alloys**
  - **A family of Cu-Cr-Nb alloys with a nearly pure Cu matrix strengthened by Cr_2Nb particles**
  - **GRCop-42 and GRCop-84 have been successfully tested and flown**
    - GRCop-42 (Cu-4 at.% Cr-2 at.% Nb) has higher thermal conductivity but slightly lower strength and life in reusable launch vehicles
    - GRCop-84 (Cu-8 at.% Cr-4 at.% Nb) trades thermal conductivity for longer life in reusable engines

Samples Examined and Build Parameters

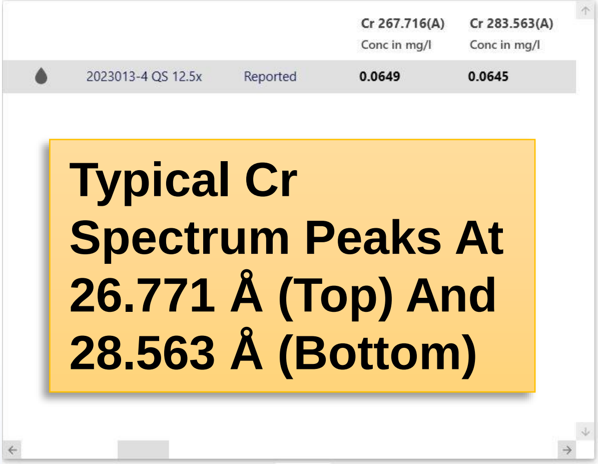
- **NASA is examining ten samples made by multiple processing routes**
  - Eight GRCop-42 and two GRCop-84 builds were examined
- **Program is measuring geometric capabilities, thermophysical properties, mechanical properties, microstructure, surface texture, and chemistries to determine effect of powder lot, machine, and build parameters**

Identifier	Alloy	Company	Machine	Layer Height (um)	Recoater	Energy Density (J/mm^3)	Scan Strategy
GRCop-42-1	GRCop-42	A	EOS M280	40	Rubber	75	Continuous
GRCop-42-2	GRCop-42	B	EOS M290	45	Steel	90.3	Stripes
GRCop-42-3	GRCop-42	B	EOS M400-1	60	Steel	83.3	Stripes
GRCop-42-4	GRCop-42	C	EOS M400-1	40	Rubber	75	Continuous
GRCop-42-5	GRCop-42	A	EOS M280	40	Steel	75	Continuous
GRCop-42-6	GRCop-42	D	EOS M290	40	Carbon Fiber Brush	N/A	N/A
GRCop-42-7	GRCop-42	E	EOS M400-4	60	Steel	83.3	Stripes
GRCop-42-8	GRCop-42	F	EOS M290	45	Carbide	90.3	N/A
GRCop-84-1	GRCop-84	G	Concept M2	30	Rubber	100	Checkered
GRCop-84-2	GRCop-84	H	EOS M290	40	Steel	107.1	Stripes

Bulk Chemical Analyses - Ametek Arcos Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

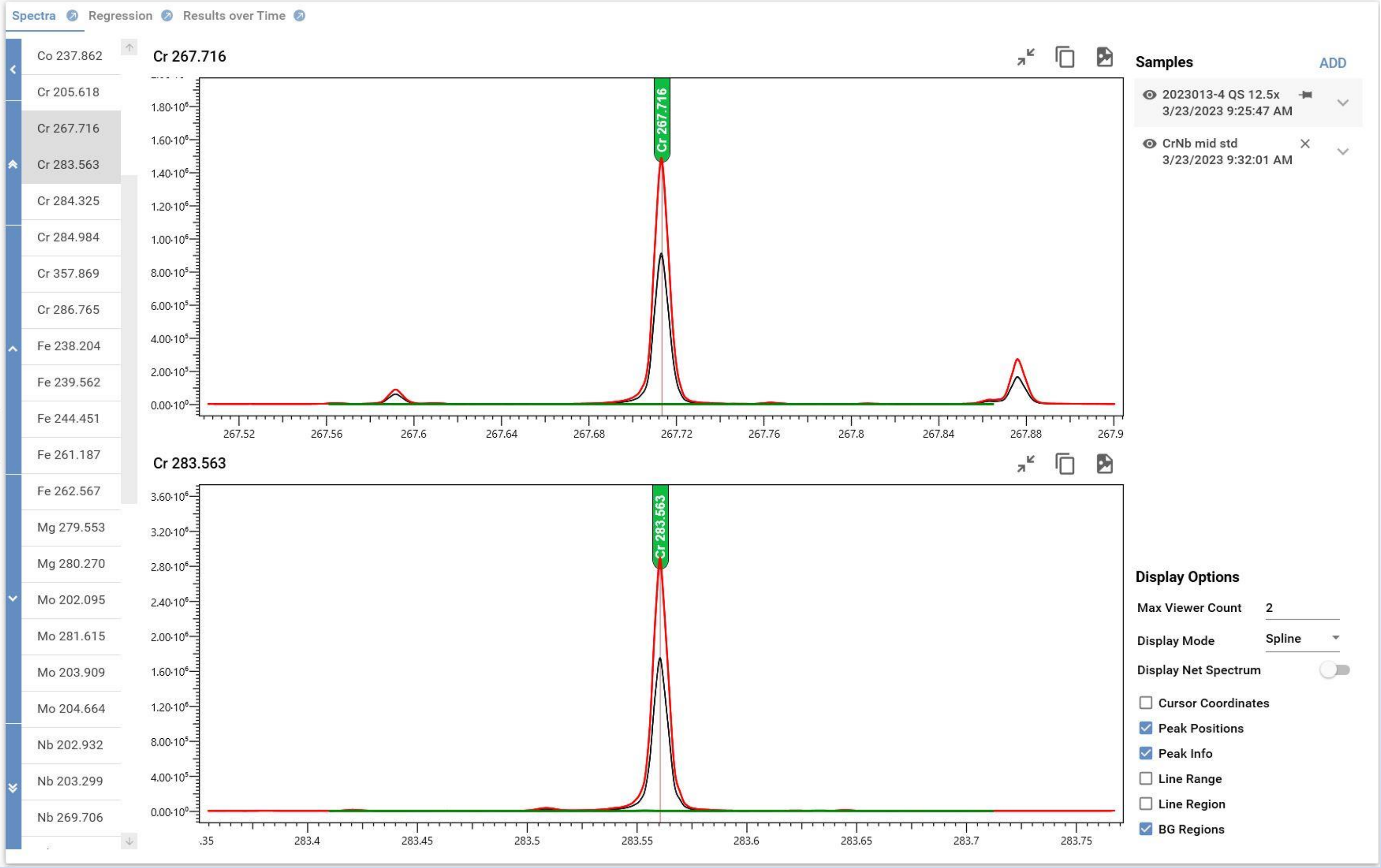
- **Ametek Arcos Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) unit used to determine metals between H and U**
  - Necessary for discovery of unknown trace elements
  - Analyzes spectra between 130 nm and 770 nm wavelengths
- **LECO 844 Series Combustion Analyzer was used for C and S**
- **LECO 736 Series Inert Gas Fusion unit was used for N and O**
  - C, S, and O are detected with non-dispersive infrared (NDIR) cells tuned to the element being measured
  - N is detected by the chenge in thermal conductivity of the gas relative to the carrier gas

Typical ICP-OES Cr Spectrum And Analysis



Typical Cr Spectrum Peaks At 26.771 Å (Top) And 28.563 Å (Bottom)

	Cr 26.771 Å	Cr 28.563 Å
	Con. (mg/l)	Con. (mg/l)
1	0.0647	0.0643
2	0.0656	0.0653
3	0.0643	0.0639
Min Cal. Tange	0.000001	0.000002
Reported	**0.0649**	**0.0645**
Max. Cal. Range	0.117	0.117
Mean	0.0649	0.0645
SD	0.000643	0.000716
RSD%	0.99%	1.11%



- **Sample spectra are compared to reference spectra**
- **Combination of wavelength, intensity, and reference spectra used to identify the elements present and quantify the amounts**
- **ICP-OES is capable of ppm level detection of metals**

Bulk Chemistries

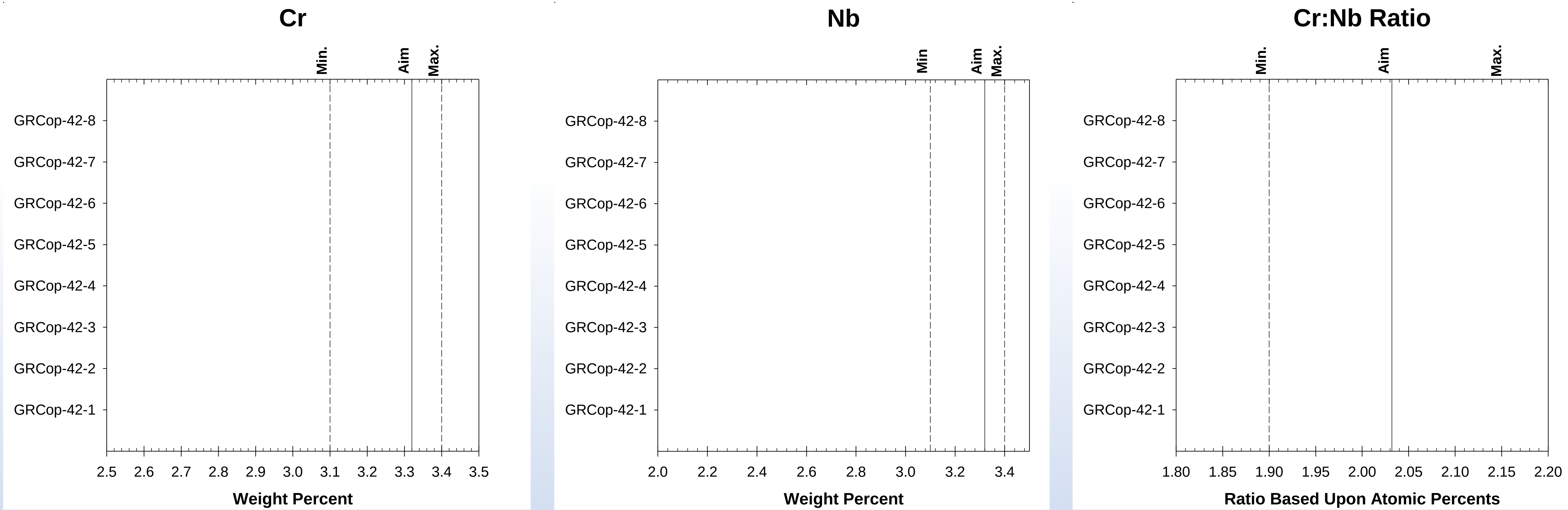
		Controlled Elements							Cr:Nb Ratio	
Alloy	Sample	Cu	Cr (wt.%)	Nb (wt.%)	Fe (ppm)	O (ppm)	Al (ppm)	Si (oom)	Weight Basis	Atomic Basis
Nominal	*Aim*	*Bal.*	*3.32*	*2.95*	*<20*	*<400*	*-*	*-*	*1.14*	*2.03*
GRCop-42	GRCop-42-1	Bal.	3.22	2.82	90	795	16	390	1.14	2.03
GRCop-42	GRCop-42-2	Bal.	3.29	2.95	70	530	10	220	1.11	1.99
GRCop-42	GRCop-42-3	Bal.	3.25	2.89	70	435	9	210	1.13	2.01
GRCop-42	GRCop-42-4	Bal.	TBD							
GRCop-42	GRCop-42-5	Bal.	3.20	2.77	90	885	21	340	1.15	2.06
GRCop-42	GRCop-42-6	Bal.	3.31	3.08	40	510	9	200	1.08	1.92
GRCop-42	GRCop-42-7	Bal.	3.16	2.75	30	710	7	110	1.15	2.05
GRCop-42	GRCop-42-8	Bal.	TBD							
GRCop-84	*Aim*	*Bal.*	*6.65*	*5.85*	*<20*	*<400*	*-*	*-*	*1.14*	*2.05*
GRCop-84	GRCop-84-1	Bal.	6.48	5.77	20	1210	9	60	1.12	2.00
GRCop-84	GRCop-84-2	Bal.	6.52	5.61	40	1175	9	310	1.16	2.08

N.D. - No detectable peak in spectrum

<X - Peak detected but concentration below lower limit of detection

		Trace Elelements							Other Interstitial Elements		
Alloy	Sample	Ag (ppm)	Co (ppm)	Mo (ppm)	Ni (ppm)	P (ppm)	Ti (ppm)	Y (ppm)	Zr (ppm)	C (ppm)	S (ppm)	N (ppm)
GRCop-42	GRCop-42-1	16	22	<50	160	50	< 10	< 1	N. D.	19	7	22
GRCop-42	GRCop-42-2	10	N. D.	N. D.	20	30	< 10	N. D.	N. D.	13	7	21
GRCop-42	GRCop-42-3	9	N. D.	N. D.	20	30	< 10	N. D.	N. D.	8	8	22
GRCop-42	GRCop-42-4	TBD										
GRCop-42	GRCop-42-5	21	21.3333	<50	150	50	< 10	113	N. D.	32	12	38
GRCop-42	GRCop-42-6	9	N. D.	N. D.	10	30	N. D.	N. D.	N. D.	13	8	23
GRCop-42	GRCop-42-7	7	14	100	50	40	40	3	7	7	8	4
GRCop-42	GRCop-42-8	TBD										
GRCop-84	GRCop-84-1	9	N. D.	N.D.	10	20	< 10	N. D.	N. D.	22	11	7
GRCop-84	GRCop-84-2	9	20	<50	10	130	< 10	N. D.	N. D.	33	13	29

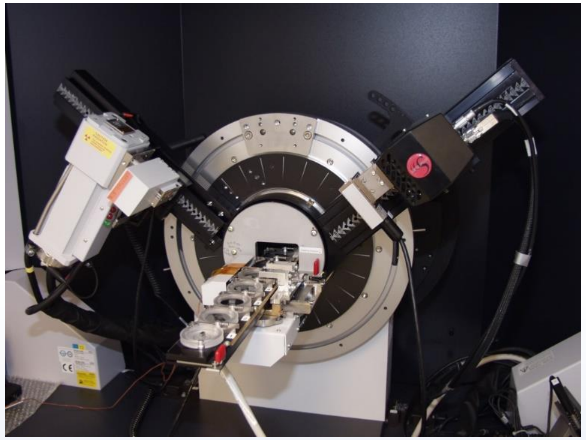
GRCop-42 Cr, Nb, and Cr:Nb Ratios Compared to Specification



- **Cr is below the aim but falls within the specification limits**
- **Nb is below lower specification limit**
  - Problems encountered dissolving Nb into melt
  - Corrected in more recent powder atomization runs
- **Cr:Nb is within specification because both Cr and Nb were low**
  - Probably have 6-6.5 vol.% Cr_2Nb instead of target 7 vol..%

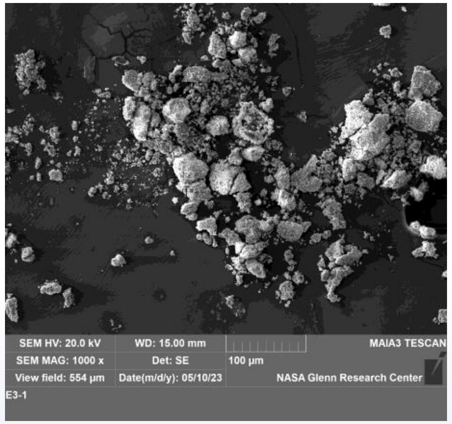
Phase Identification:
X-ray Diffraction (XRD) Of Extracted Particles

- **Particles first extracted to concentrate them and make detection of minor phases easier**
  - Cu dissolved with concentrated nitric acid
  - Remaining particles filtered through 0.45 μm filter paper
- **Bruker D8 Advance diffractometer used for XRD**
  - Cu K_α radiation
  - Small step size and long dwell time for maximum S/N
- **JADE software used to implement whole pattern fitting (WPF, aka, Rietveld refinement)**
  - Allows quantitative measurement of phases present

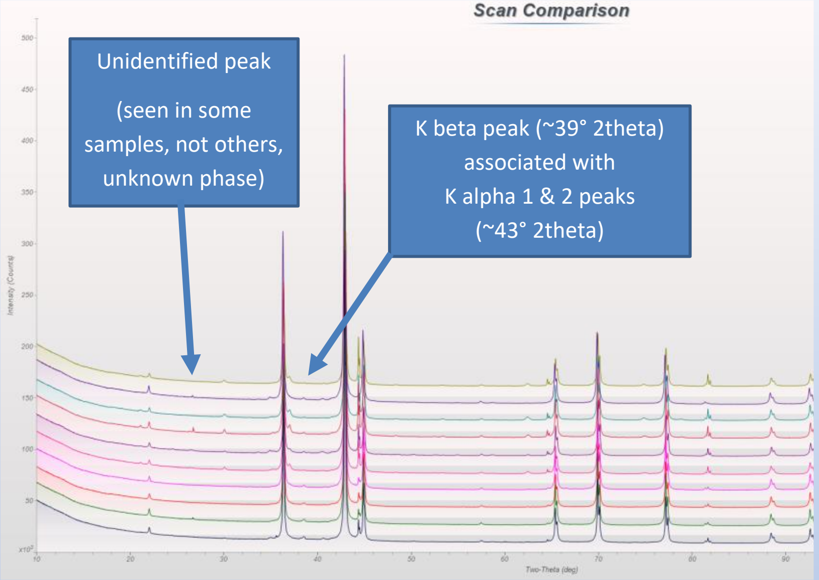


D8 goniometer (above) and unit (below)

XRD Phase Analyses



Example of particles



XRF Spectra

Sample	Alloy	Total (wt.%)	Cr_2Nb	Cr	NbO†	Cu_2O
GRCop-42-1	GRCop-42	6.83	83.9	7.3	-	5.5
GRCop-42-2	GRCop-42	7.12	90.7	8.7	0.6	
GRCop-42-3	GRCop-42	7.26	94.4	5.6		
GRCop-42-4	GRCop-42	6.05	93.5	5.6	-	1.9
GRCop-42-5	GRCop-42	6.27	74.7	23.6		1.7
GRCop-42-6	GRCop-42	4.92	74.7	23.6		1.7
GRCop-42-7	GRCop-42	7.55	86.2	7.8	6.0	
GRCop-42-8	GRCop-42	7.17	94.0	6.0		
	Average	**6.64**	86.5	11.0		
	Nominal Cr_2Nb	**6.1**				
GRCop-84-1	GRCop-84	12.69	82.7	10.0	7.3	
GRCop-84-2	GRCop-84	12.70	81.4	11.2	7.5	
	Average	**12.70**	82.1	10.6		
	Nominal Cr_2N	**12.3**				

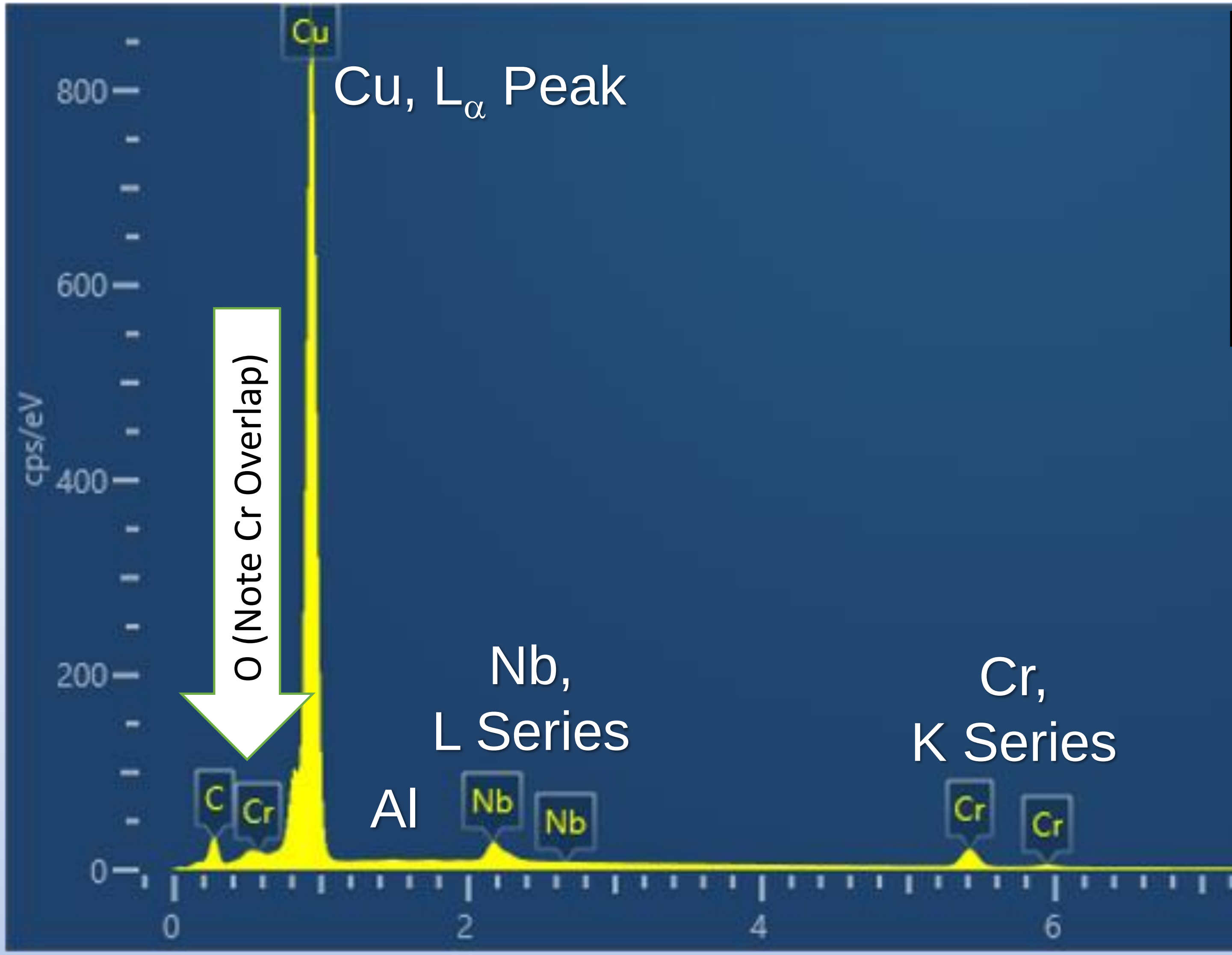
†NbO in Samples GRCop-42-1 and GRCop-42-4 not reported due to poor peak fit

TESCAN MAIA-3 Field Emission Scanning Electron Microscope (FESEM) With EDS and EBSD Capabilities

- **FESEM operated at 20 kV to provide EDS data for Nb (Kα=16.581 keV) and strong EBSD patterns**
- **Energy Dispersive Spectroscopy (EDS)**
  - Oxford X-MAX 50 EDS mapped macroscopic chemical compositions
- **Electron Backscattered Diffraction (EBSD)**
  - Oxford Nordlys Nano unit mapped phases and crystallographic data
- **Data analysis was conducted using Oxford Instruments AZtec software**

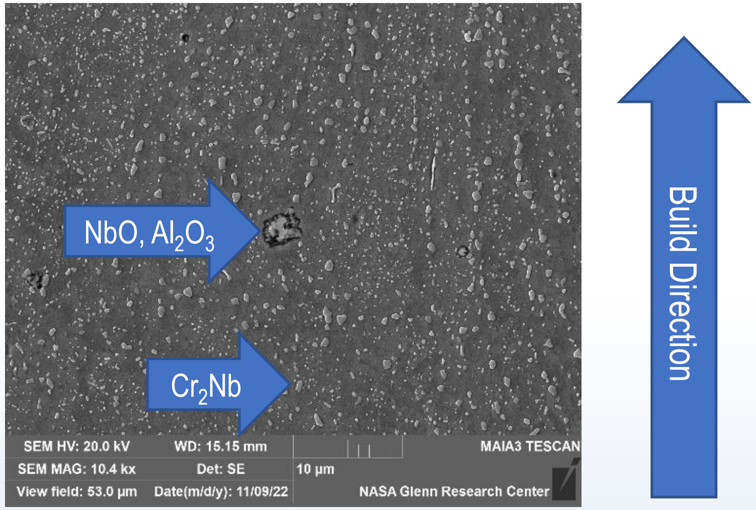
TESCAN MAIA-3 SEM at NASA GRC

Typical EDS Spectrum For Mounted GRCop-42 Sample

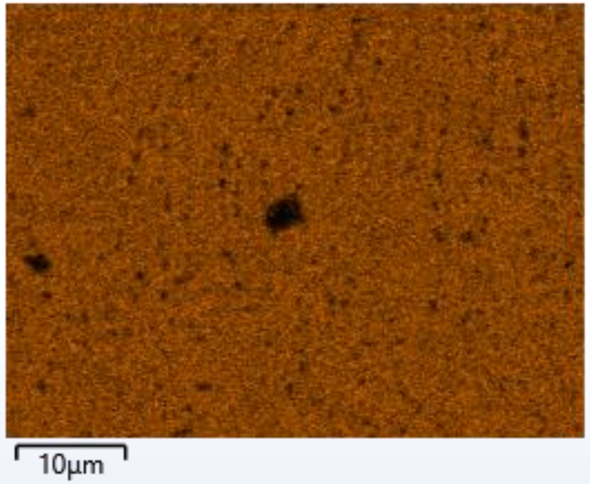


Element	wt. %	σ
Cu	91.4	0.0
Cr	4.4	0.0
Nb	4.2	0.0

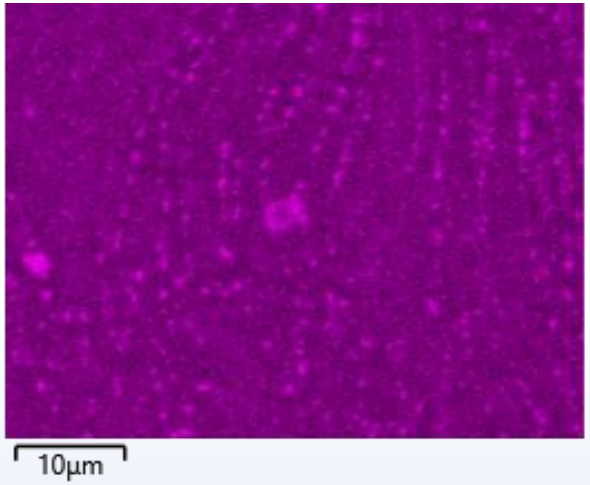
Typical Mounted Sample EDS TruMap X-ray Maps



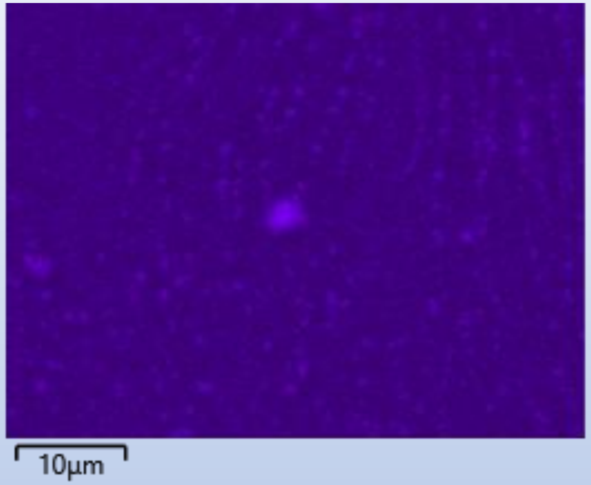
Secondary Electron (SE) Image



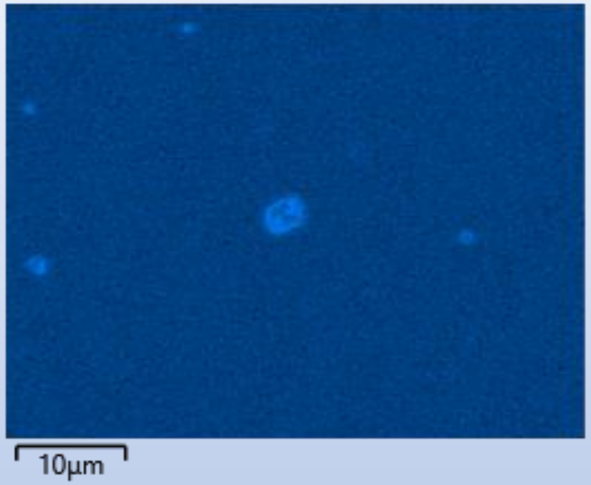
Cu, K Series



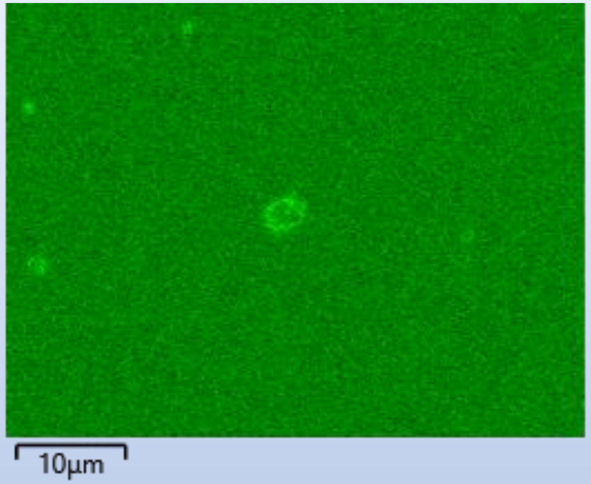
Cr, K Series



Nb, L Series

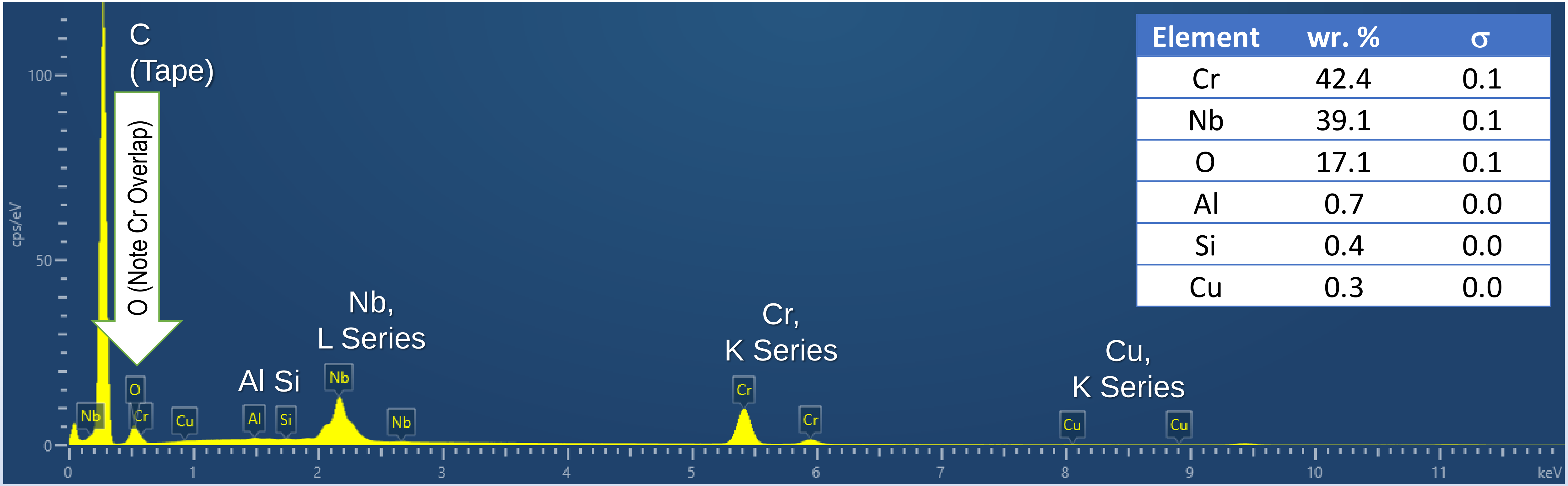


Al, K Series



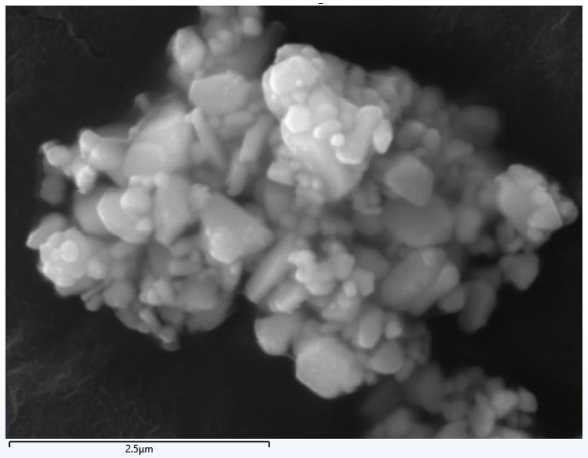
O, K Series

Typical EDS Spectrum For Extracted Particles

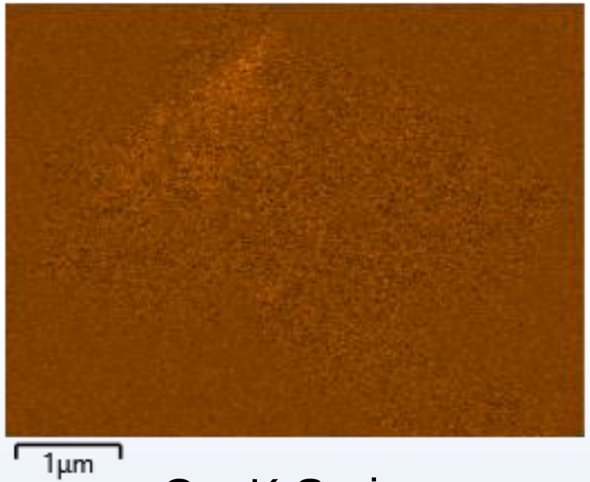


Element	wr. %	σ
Cr	42.4	0.1
Nb	39.1	0.1
O	17.1	0.1
Al	0.7	0.0
Si	0.4	0.0
Cu	0.3	0.0

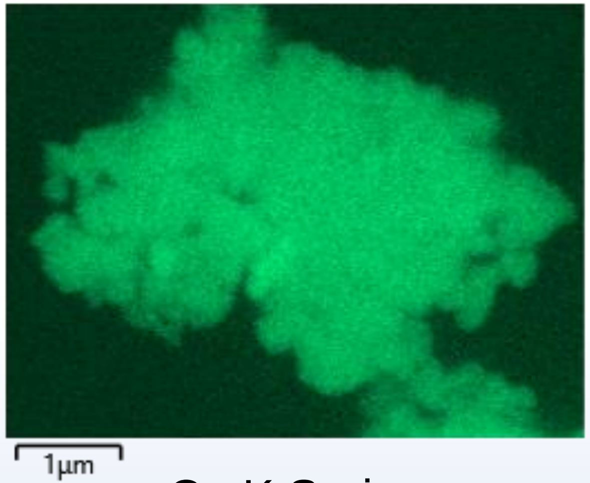
Typical Particle EDS TruMap X-ray Maps



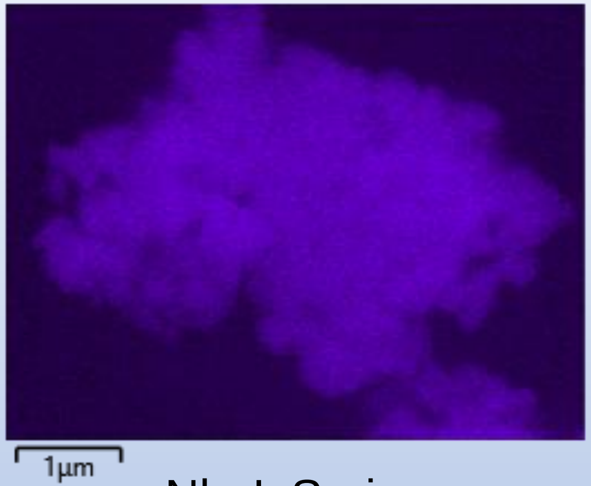
Secondary Electron (SE) Image



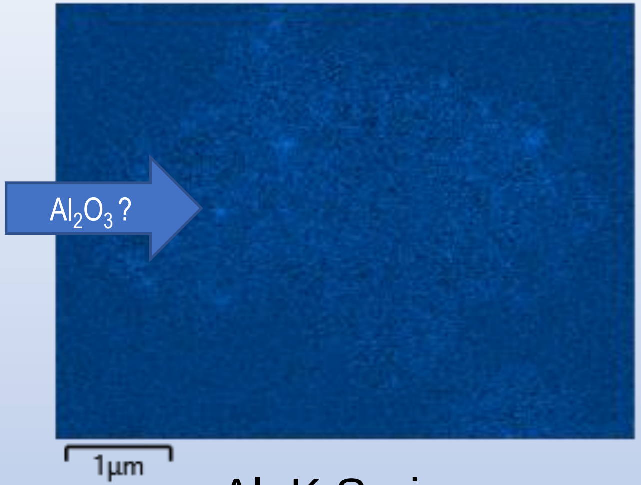
Cu, K Series



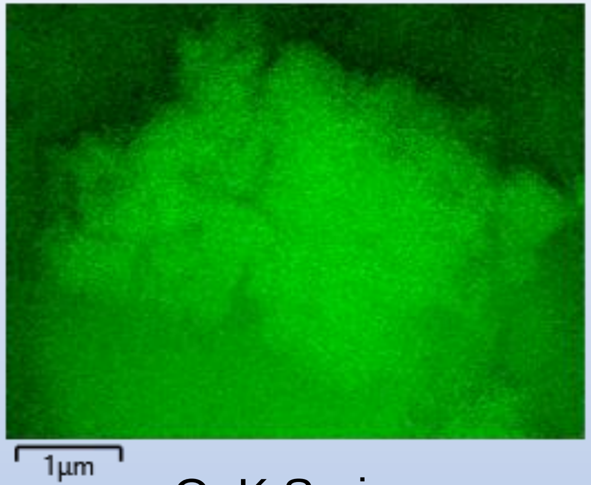
Cr, K Series



Nb, L Series



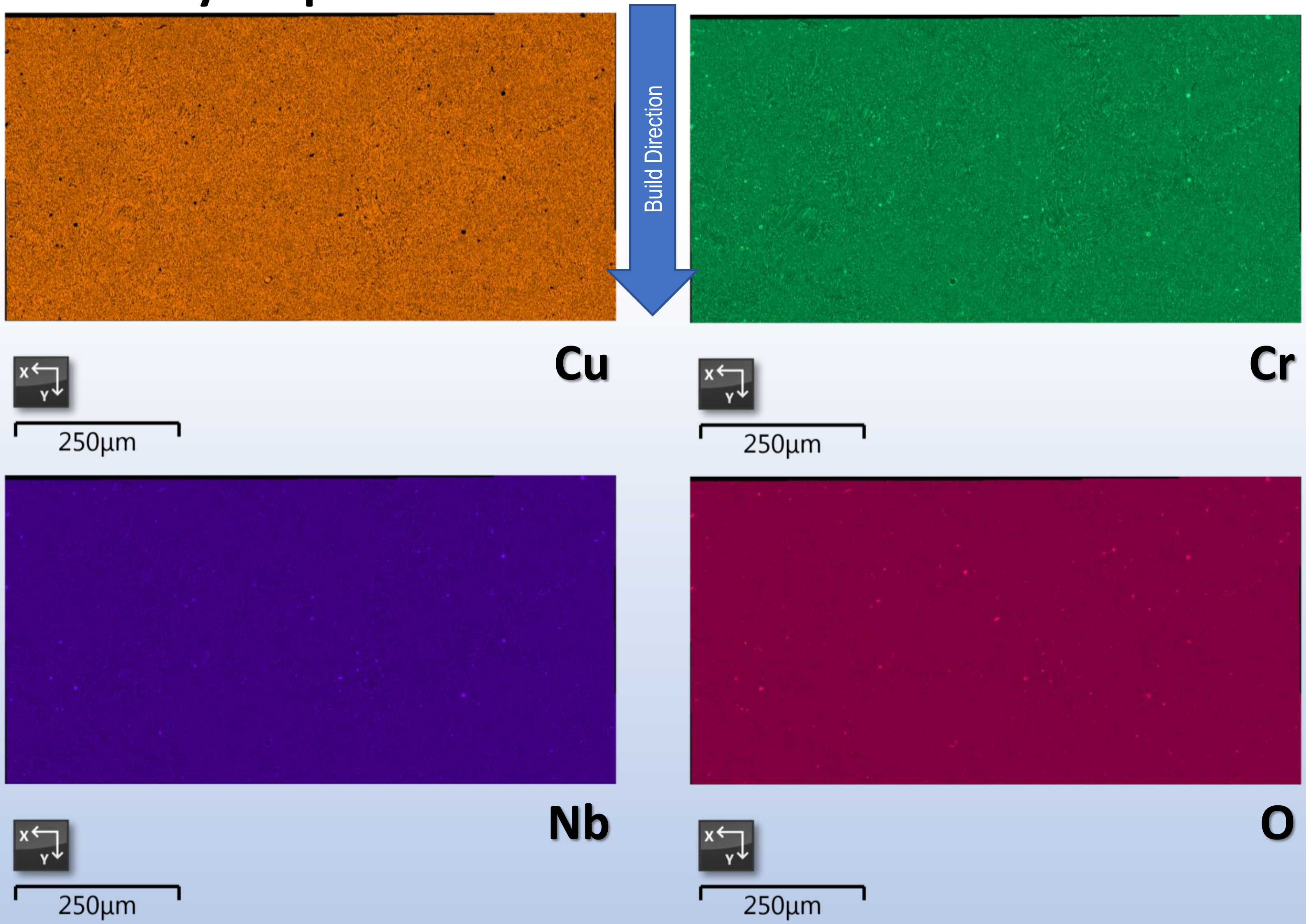
Al, K Series



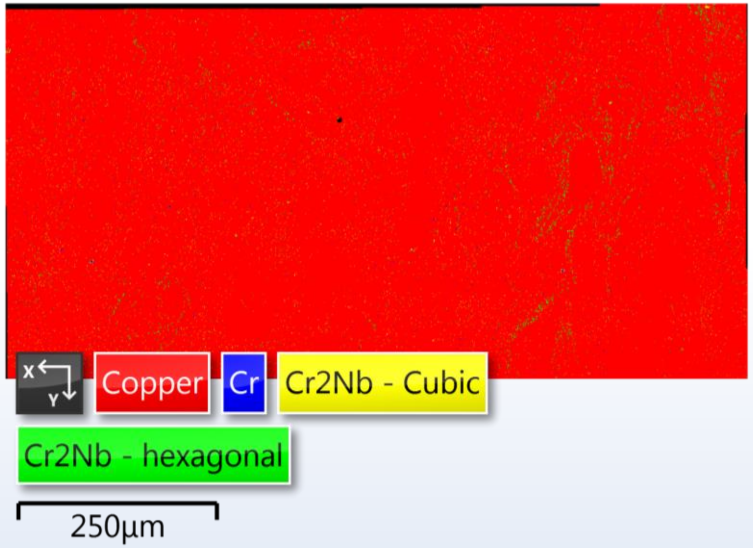
O, K Series

EDS X-ray and EBSD Phase Maps

EDS X-ray Maps



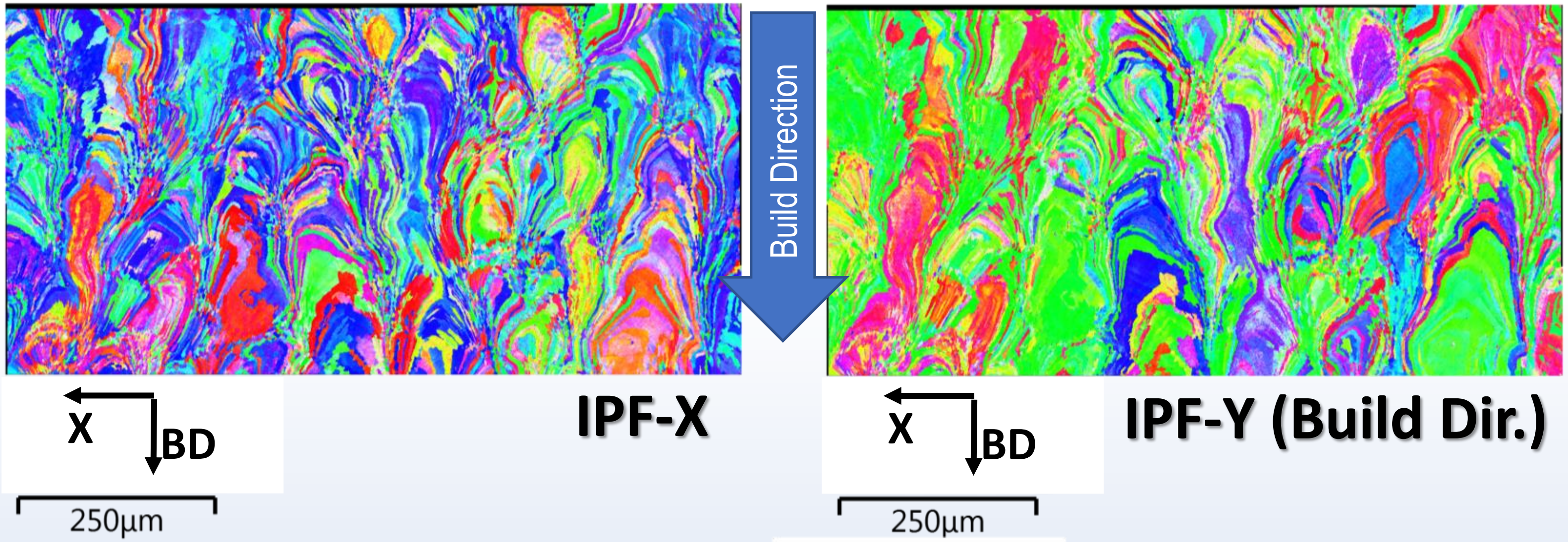
EBSD Phase Map



Phase Name	Phase Fraction (%)
Cu	97.87
Cr	0.22
Cr_2Nb FCC C15	0.64
Cr_2Nb Hex. C14	1.26
Zero Solutions	0.01

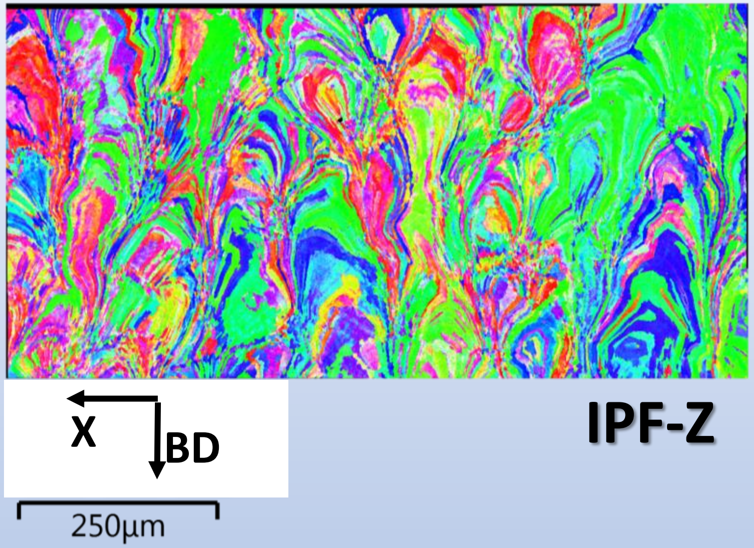
EBSD Inverse Pole Maps And Pole Figures For Typical HIPed GRCop-42 Sample

IPF Orientation Maps

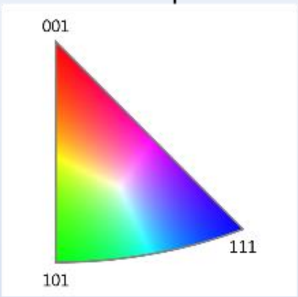


IPF-X

IPF-Y (Build Dir.)

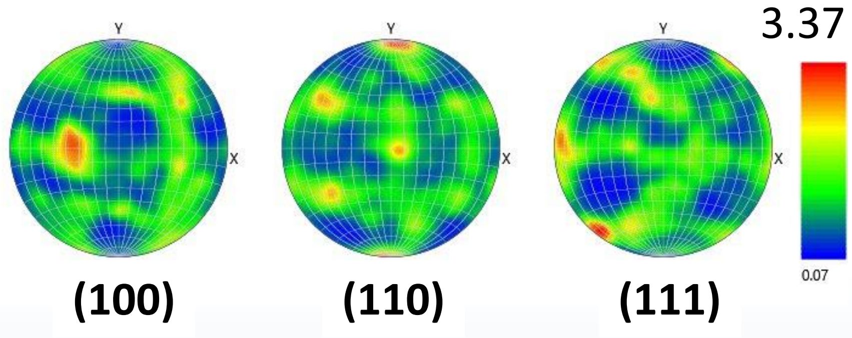


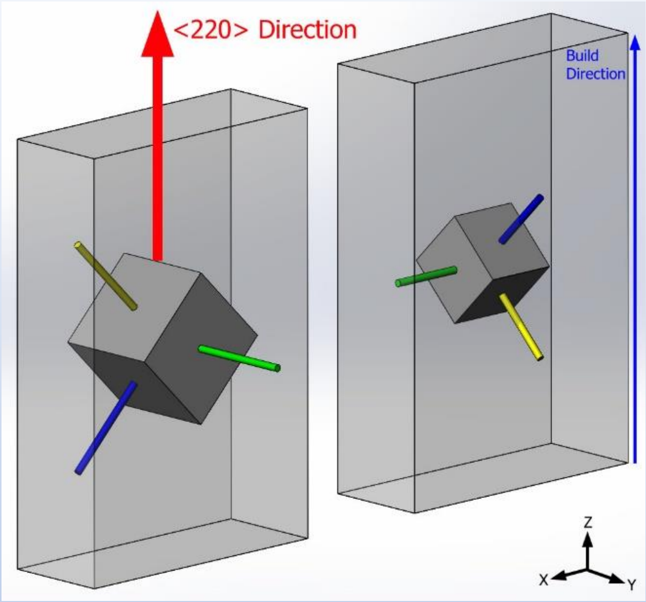
IPF-Z



The IPF-Y map indicated a strong crystallographic orientation in the Y direction, the build axis

Pole Figure

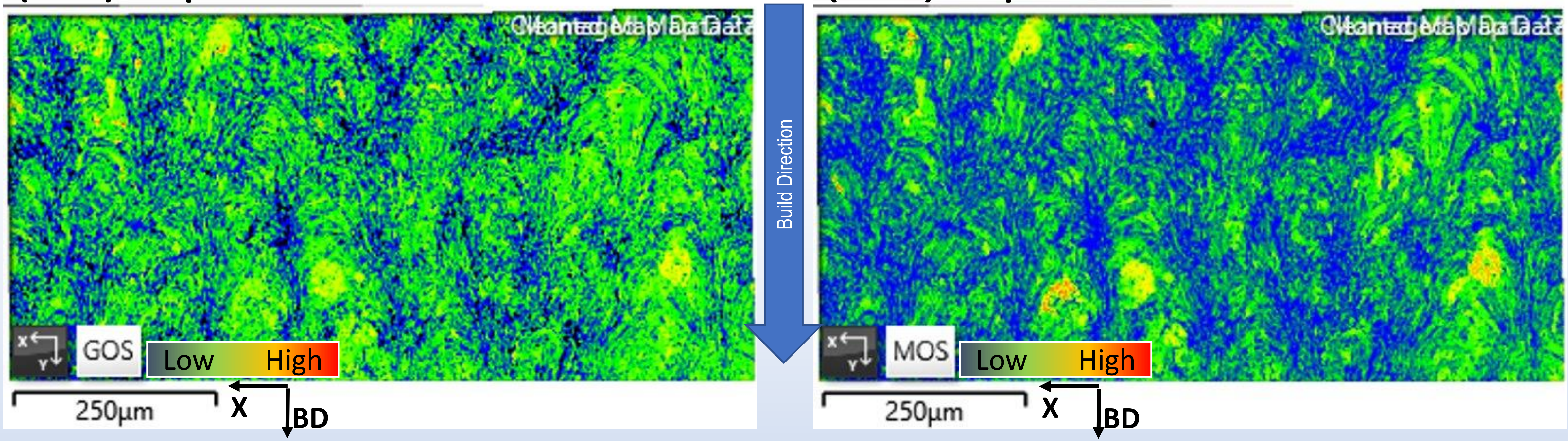




Typical Cu Residual Strains In HIPed GRCop-42

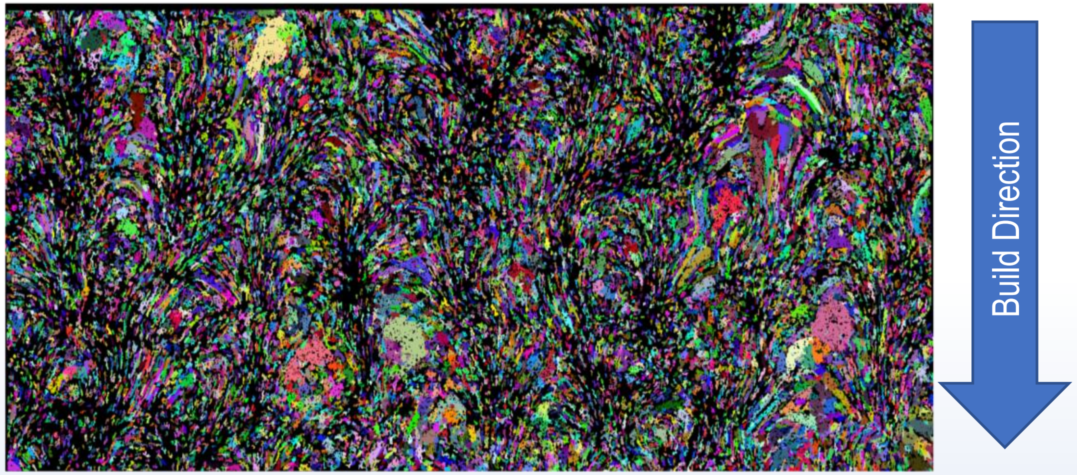
Grain Orientation Spread (GOS) Map

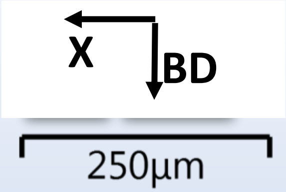
Maximum Orientation Spread (MOS) Map



- **Heat color maps indicate the degree of residual strain and by inference residual stresses**
- **Two measures of strain were calculated**
  - GOS calculates the average orientation of the grain, compares every pixel's orientation to the average, and determines the mean difference giving the average deformation in a grain
  - MOS is similar to GOS but uses the maximum difference within a grain rather than the average
- **Higher values (yellows and reds) indicate more strain and hence higher residual stresses**
- **Results indicate HIPing successfully recrystallized the Cu grains but new grains retained strong texture**

Cu Grain Size And Morphology In HIPed GRCop-42 Sample





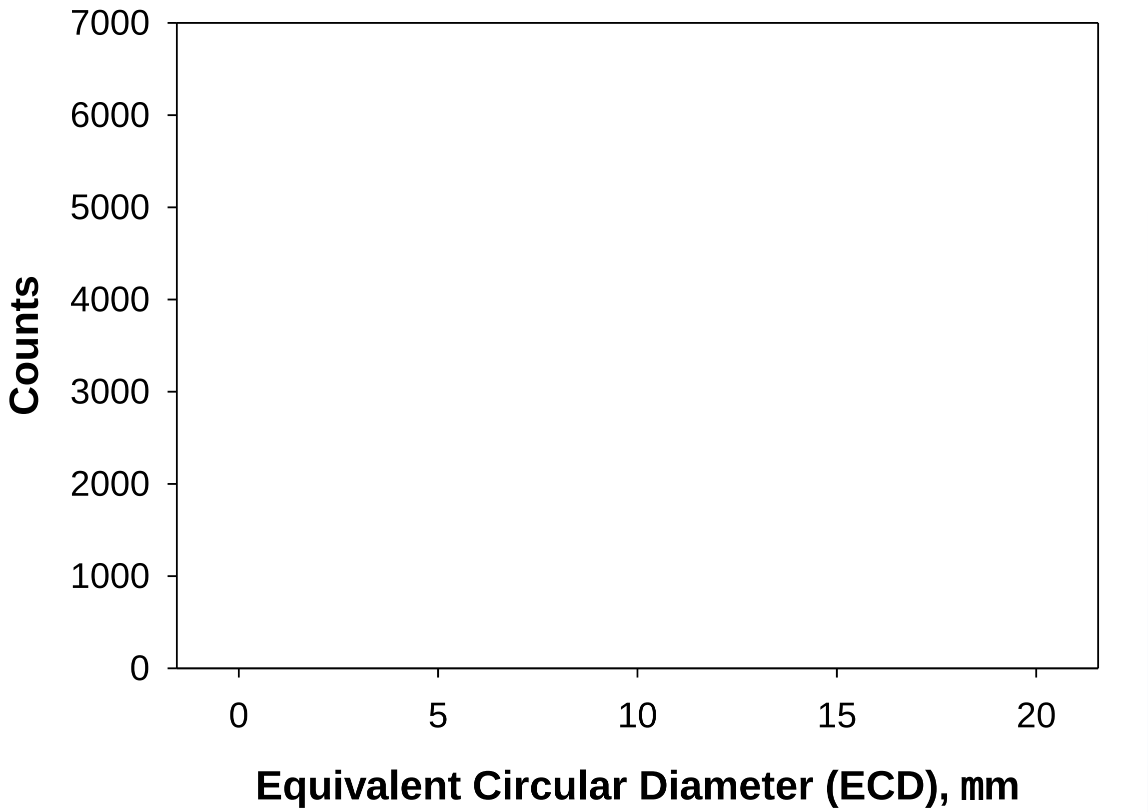
Minimum grain – 10 pixels
Minimum grain boundary angle - 3°

Measurement	Minimum	Maximum	Mean	Standard Deviation
Area (μm^2)	6.4	1,329.28	15.93	27.47
Aspect Ratio	1.04	11.32	2.2	0.88
Breadth (µm)	0.8	44.96	3.65	1.76
ECD (µm)	2.85	41.14	4.15	1.76
GOS (°)	0.52	4.13	1.71	0.42
Length (µm)	3.58	76.56	7.7	4.18
MOS (°)	0.91	11.51	3.36	1.08
Perimeter (µm)	8.84	650.07	20.68	17.89
Slope (°)	2.81	175.78	85.48	37.92

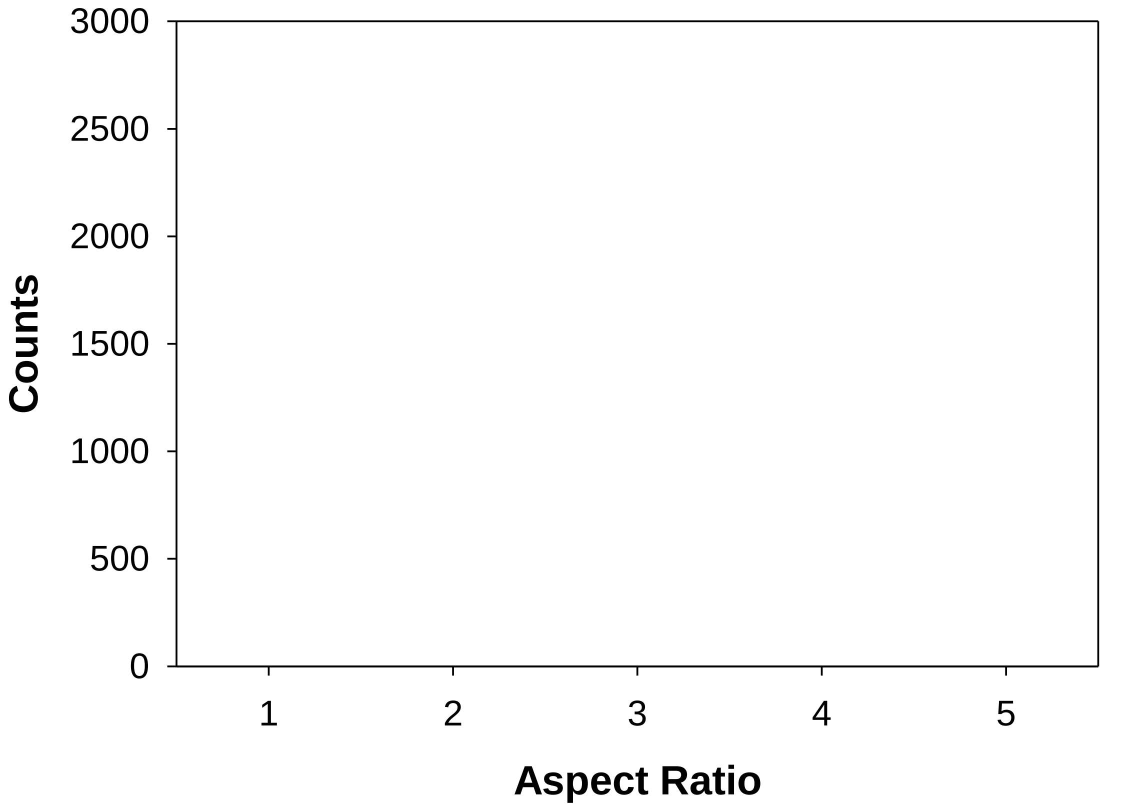
- **Many pixels were not successfully indexed**
- **Potential causes:**
  - Secondary phases
  - Very fine grains
  - Grain boundaries
- **The results are still likely representative of most Cu grains**

Selected Histograms Of Cu Grain Measurements

Equivalent Circular Diameter (ECD)



Aspect Ratio

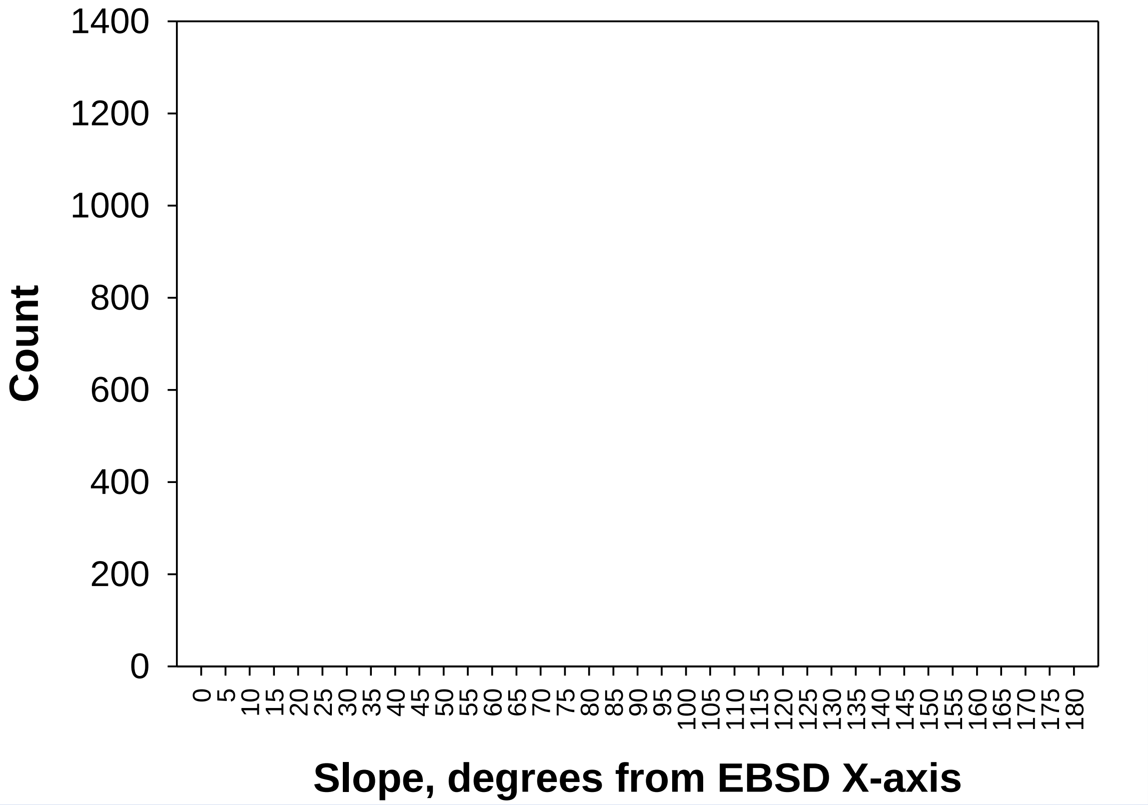


- There may be smaller grains than detected using 10 pixels
- Would need smaller step size in EBSD to resolve them

- Grains are elongated based upon the aspect ratio

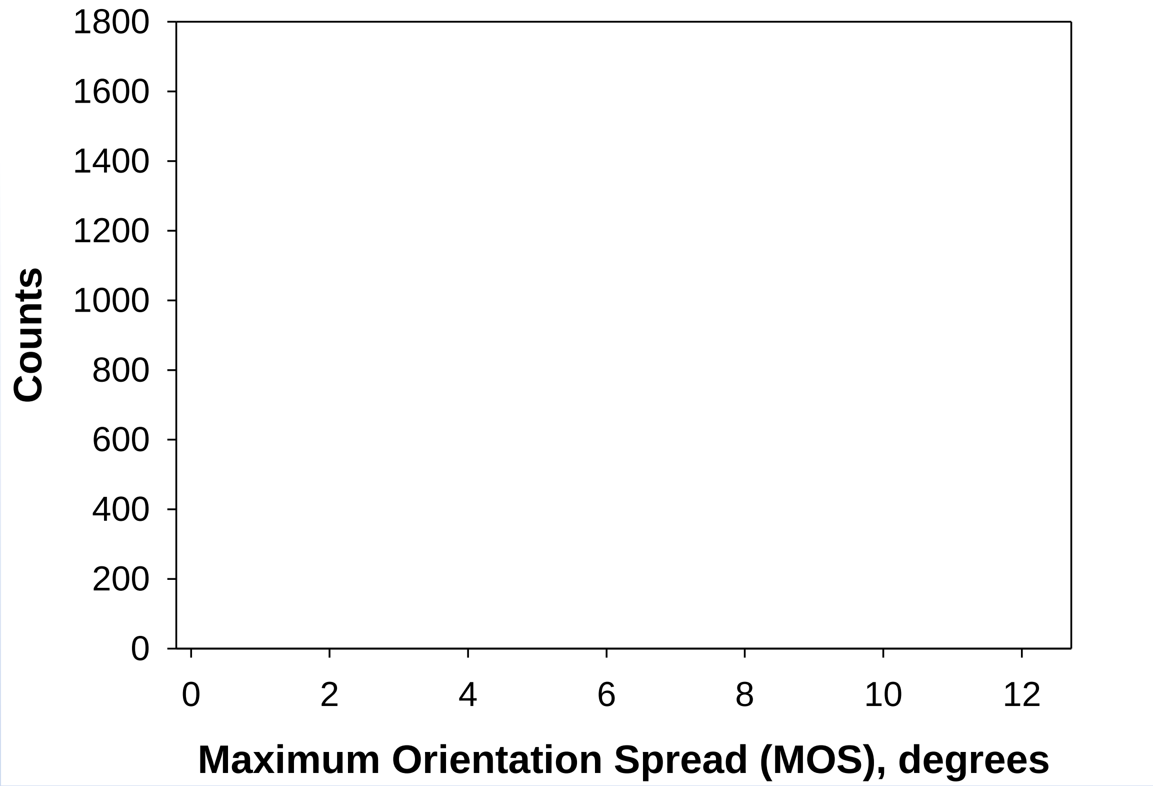
Selected Histograms Of Cu Grain Measurements (Cont.)

Slope



- Unusual notches in slope histogram noted
- More work is needed to understand this phenomenon

Maximum Orientation SPread (MOS)



- Small MOS angles indicate low strains and low residual stresses
- Highest MOS grains retain some residual stresses but are minimal in number

Summary

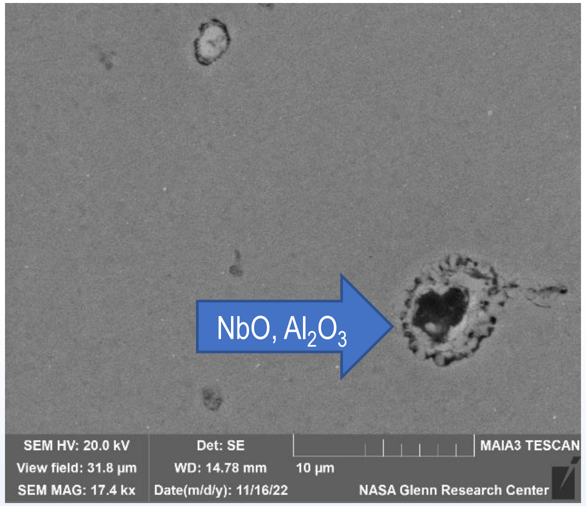
- A combination of spectroscopic and other techniques was used to characterize AM L-PBF GRCop alloys produced on multiple build platforms using different powder lots, machine setups, and processing parameters
- The results showed the bulk chemistries were similar but did have varying Cr:Nb ratios and other minor differences
- Phase extraction and XRD gave quantitative values of the phases present and revealed NbO as a ceramic inclusion
- EDS revealed that there was a nearly pure Cu matrix with Cr_2Nb, Cr, NbO, and Al_2O_3 particles. Al_2O_3 was not observed in XRD because it was encapsulated in the NbO.
- EBSD revealed a crystallographically textured, fine grained, columnar Cu grain structure even after a HIP cycle that recrystallized the Cu grains

Conclusions

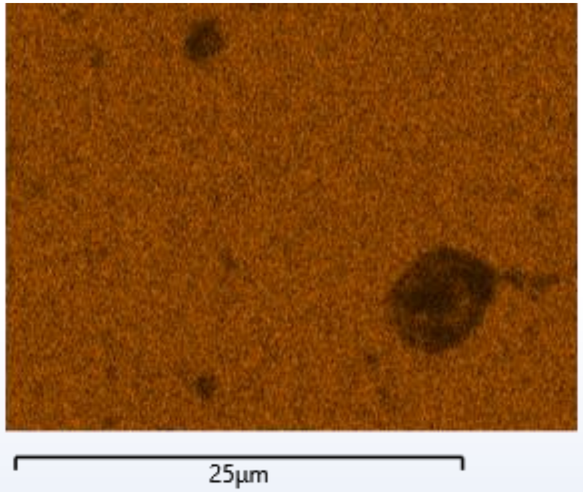
- **Spectroscopic techniques such as ICP-OES, XRD and EDS can make significant contributions to characterizing and understanding AM materials**
- **Adding other techniques in parallel such as EBSD can add additional information that can lead to a detailed understanding of results such as mechanical property anisotropy**

Backup Slides

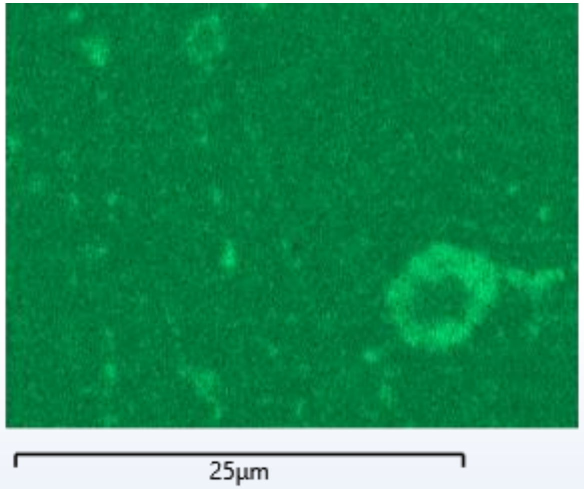
EDS X-Ray Maps For Ceramic Inclusions



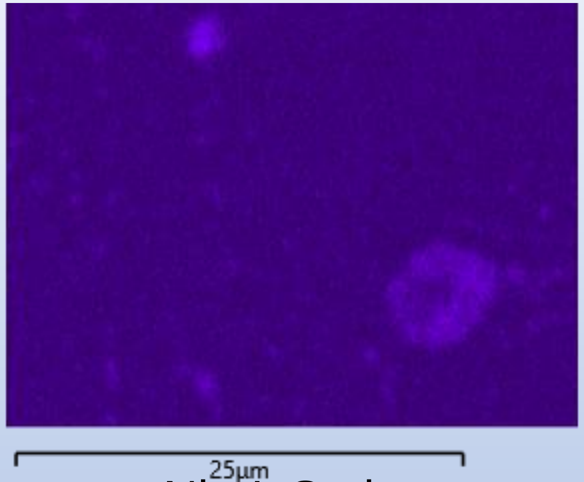
Secondary Electron (SE) Image



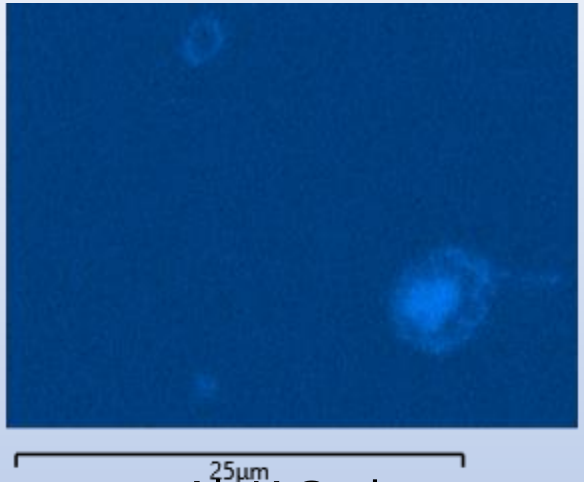
Cu, K Series



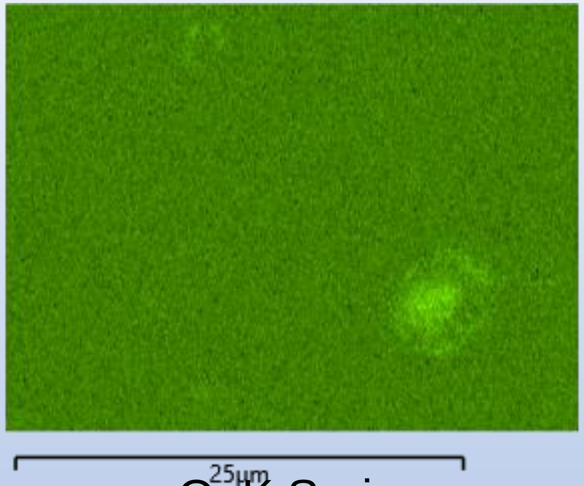
Cr, K Series



Nb, L Series



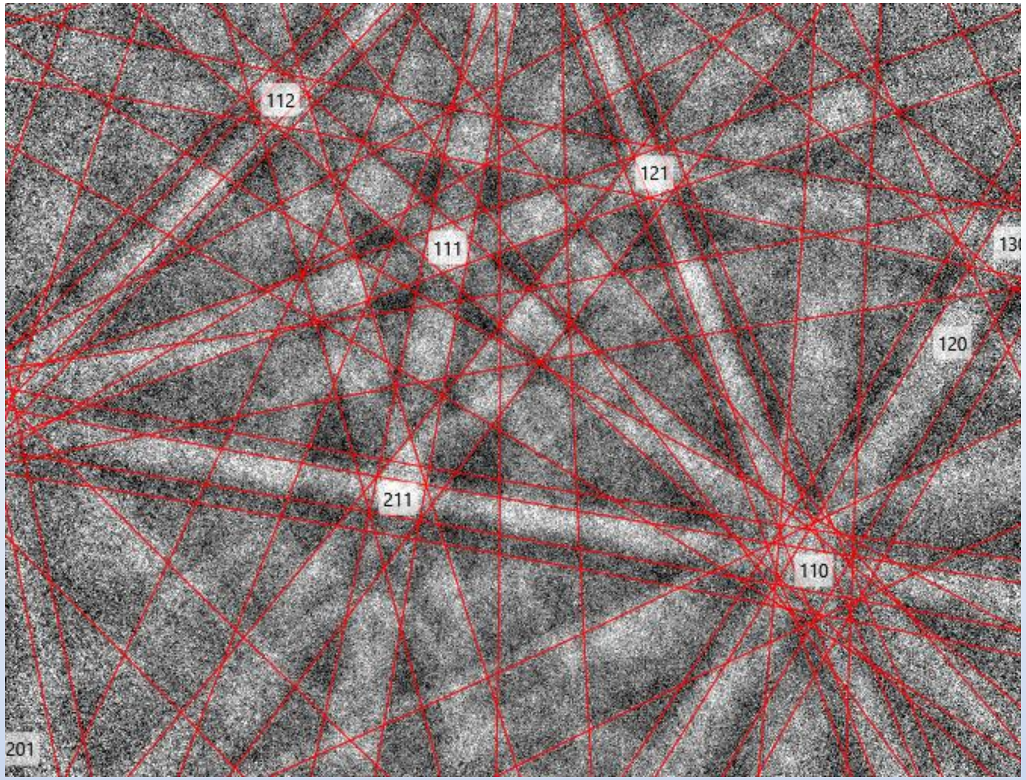
Al, K Series



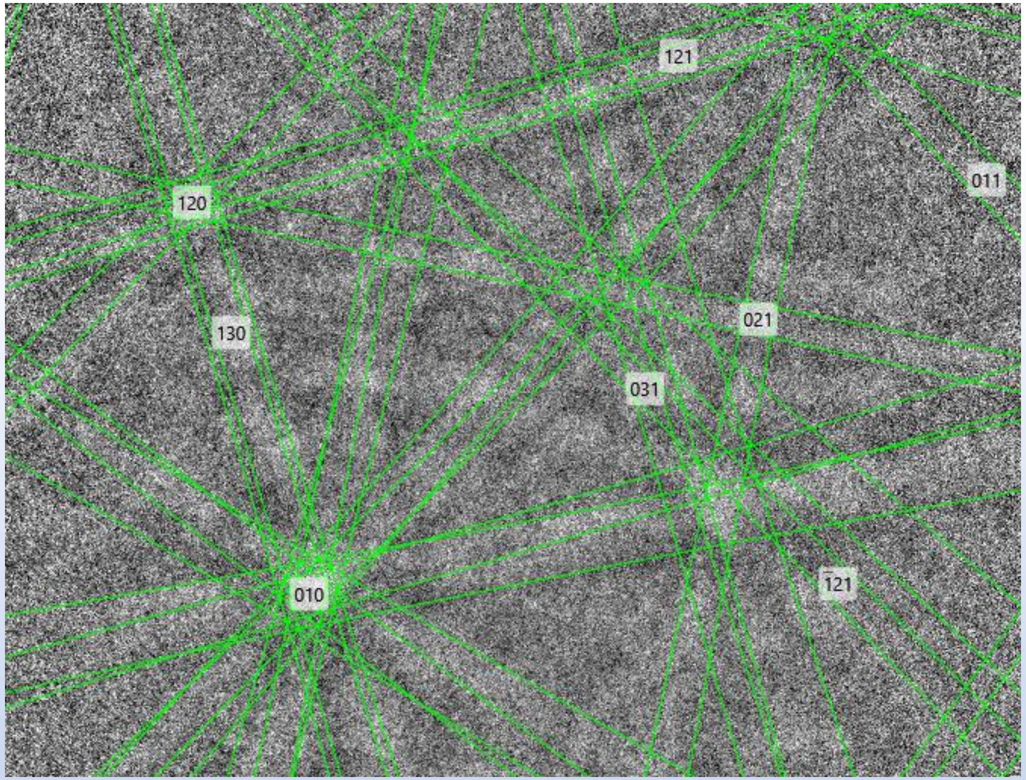
O, K Series

Representative EBSD Kikuchi Patterns

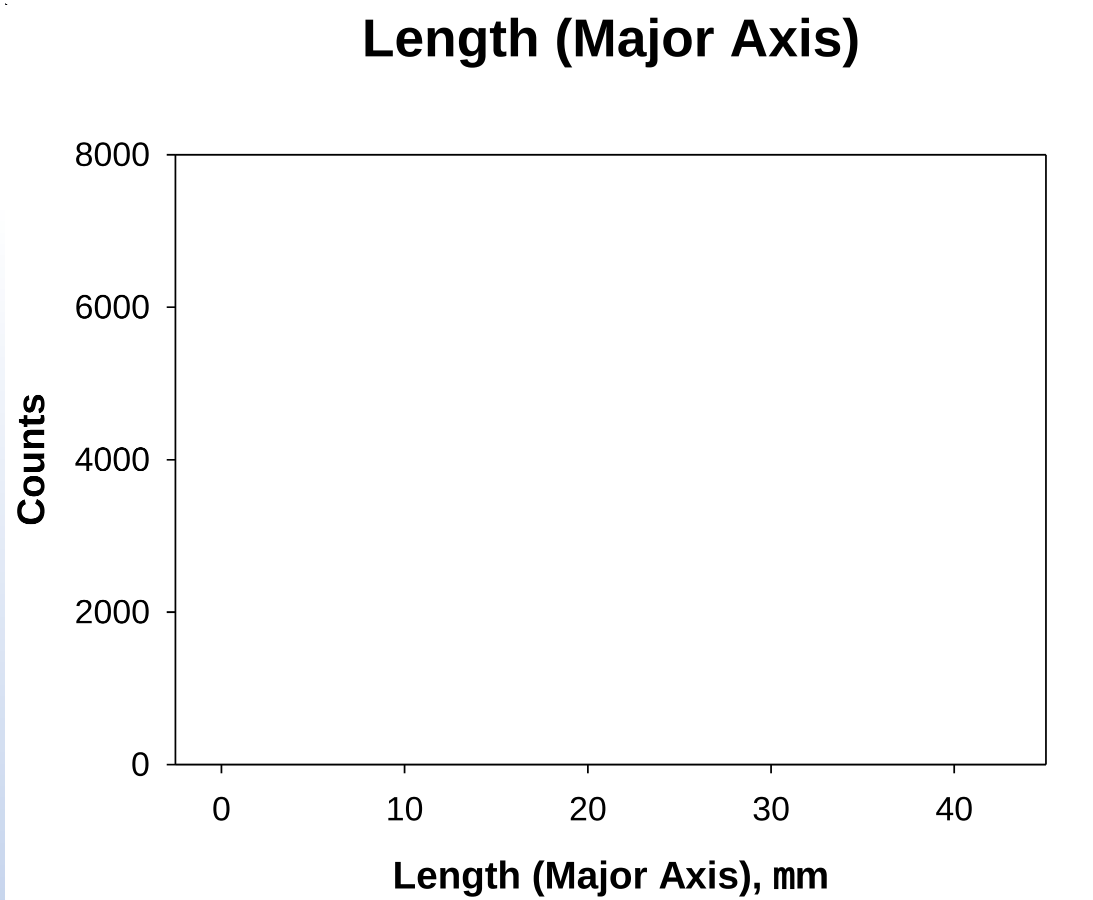
Cu

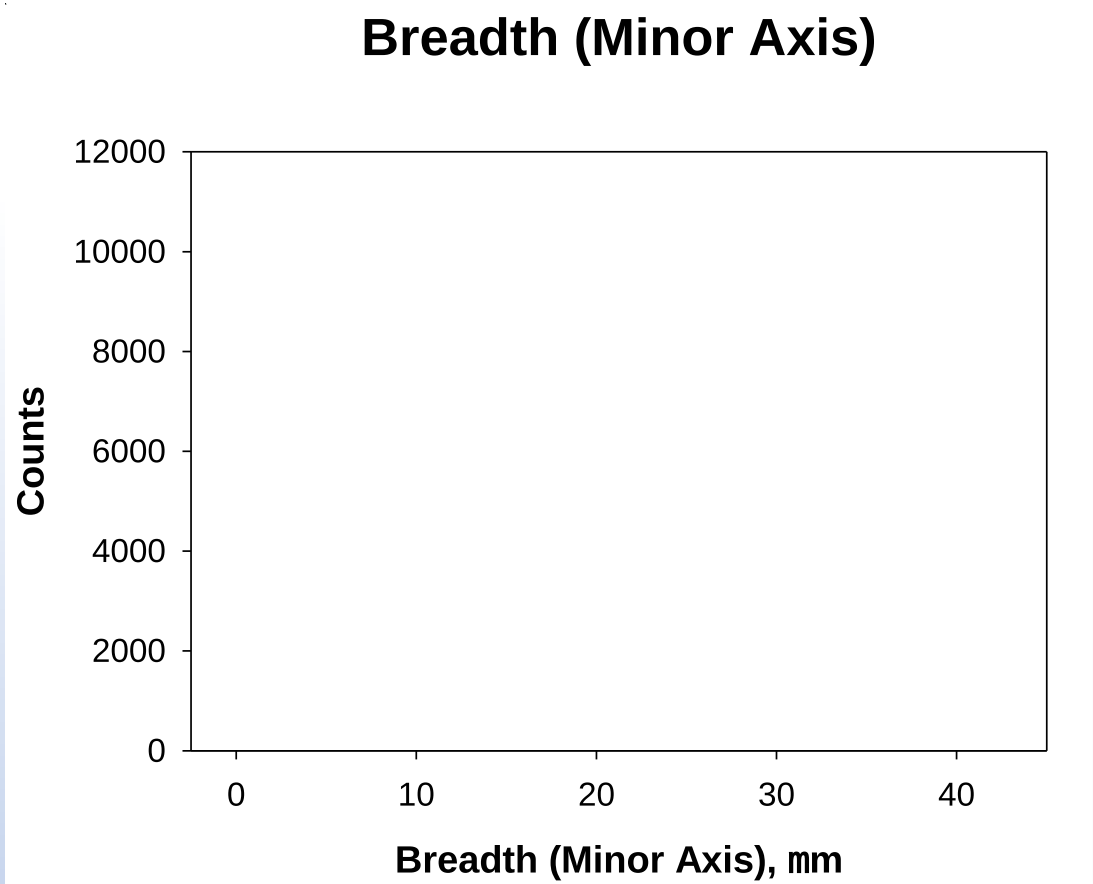


Cr_2Nb, C15 FCC

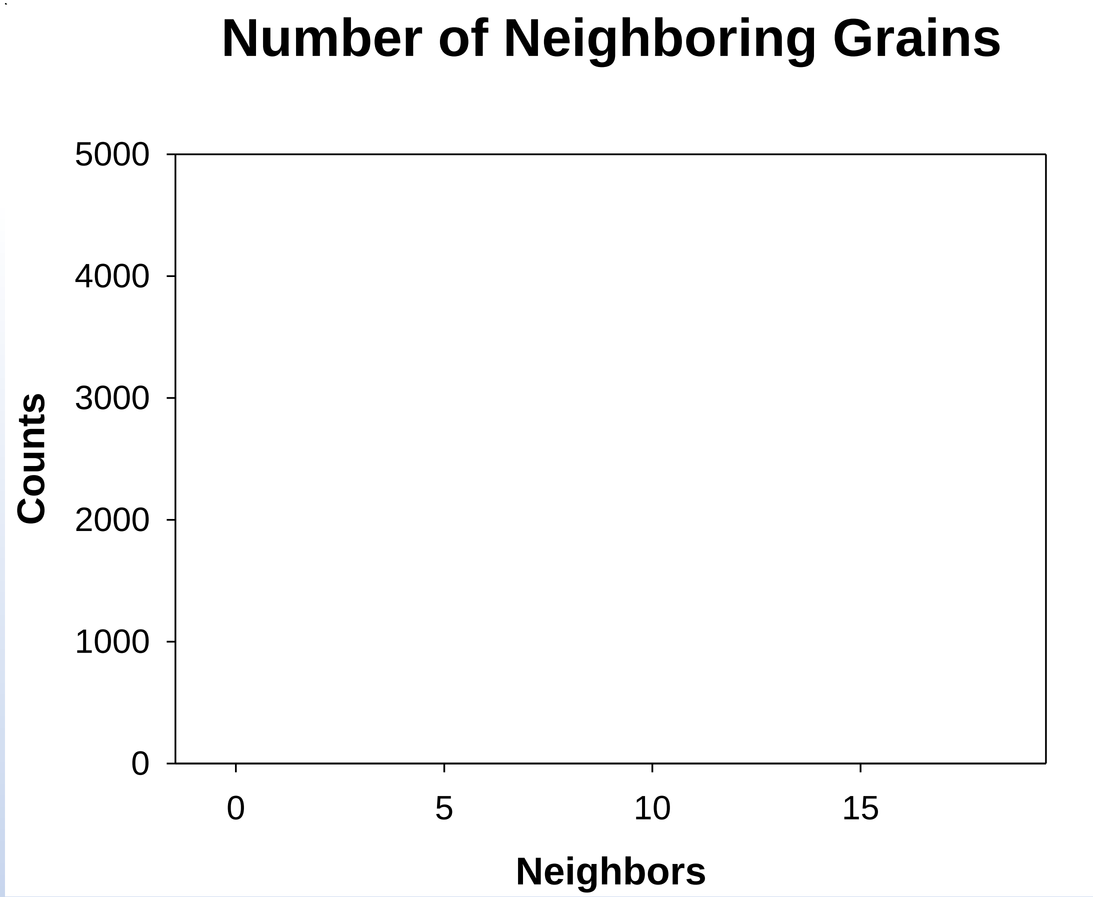


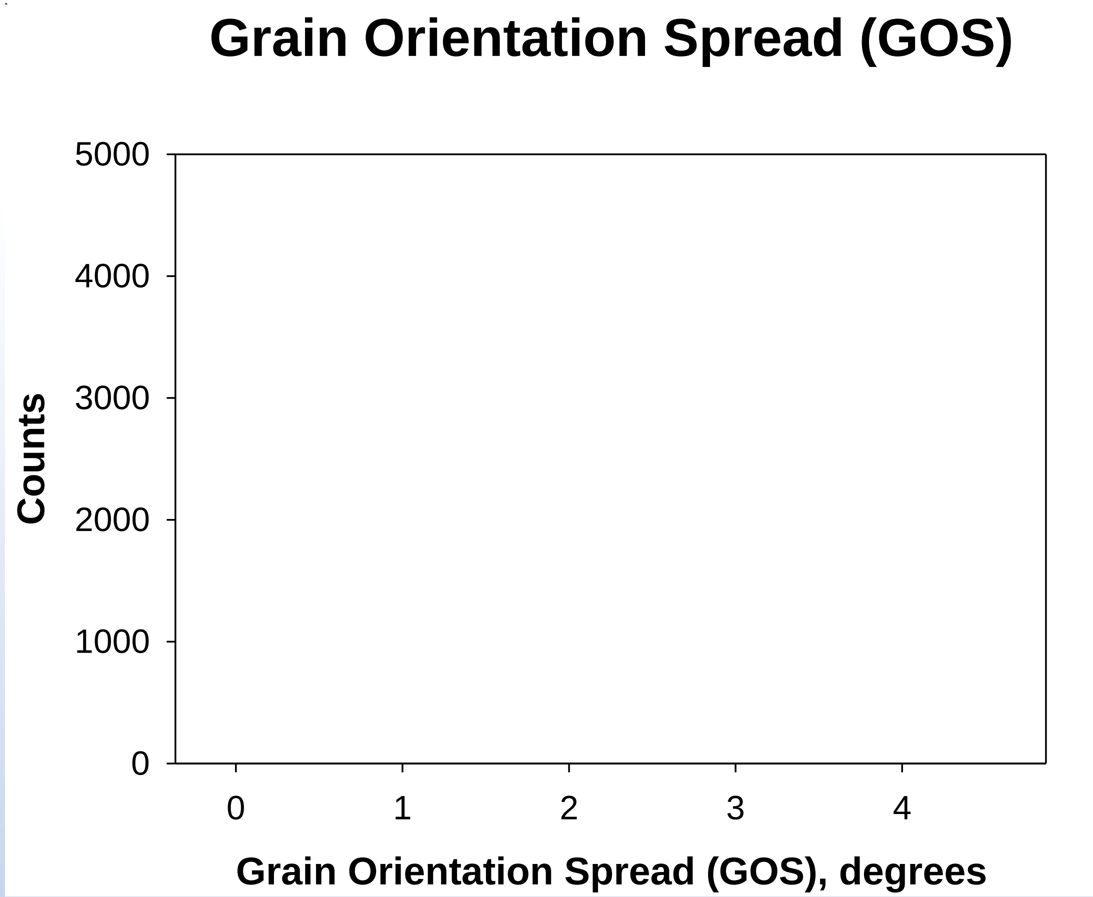
Cu Grain Size Distributions





Neighbors and
Grain Orientation Spread (GOS)





Grain Slope - 1° Bins