Serrated Plastic Flow in High Entropy Alloys

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U.S. DEPARTMENT OF ENERGY | National Energy Technology Laboratory

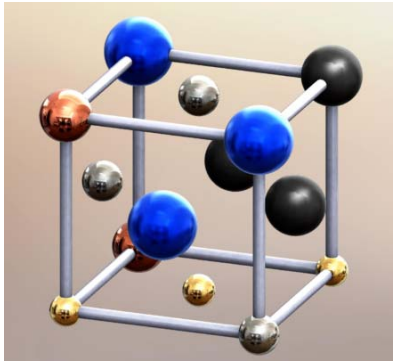
Crosscutting Review Meeting, 4/19/2016

High Entropy Concept

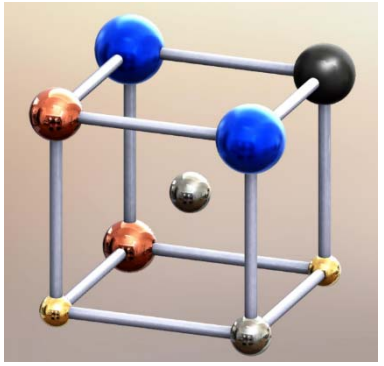
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta S_{conf} = -R\sum_{i=1}^{N} x_i \ln x_i$$

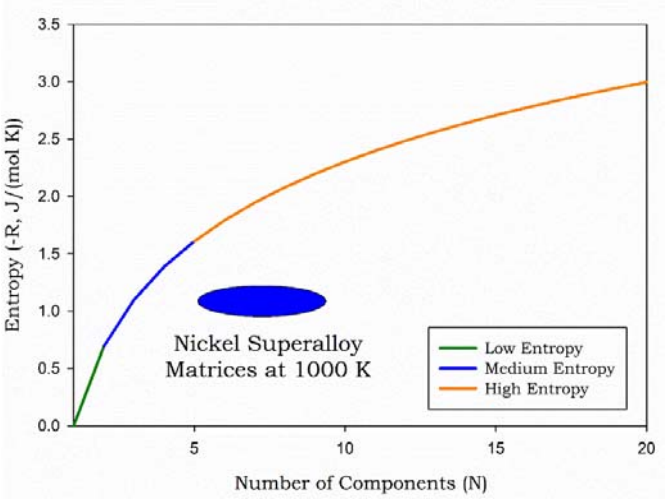
- **Multicomponent (N>4) systems**
- **Each component between 5-35 at.%**
- **Configurational entropy term decreases Gibbs energy**
  - Stabilizes single phase
  - Random lattice site occupancy
- **Resultant phase has unique properties**
- **Somewhat similar to nickel superalloys**



FCC HEA



BCC HEA



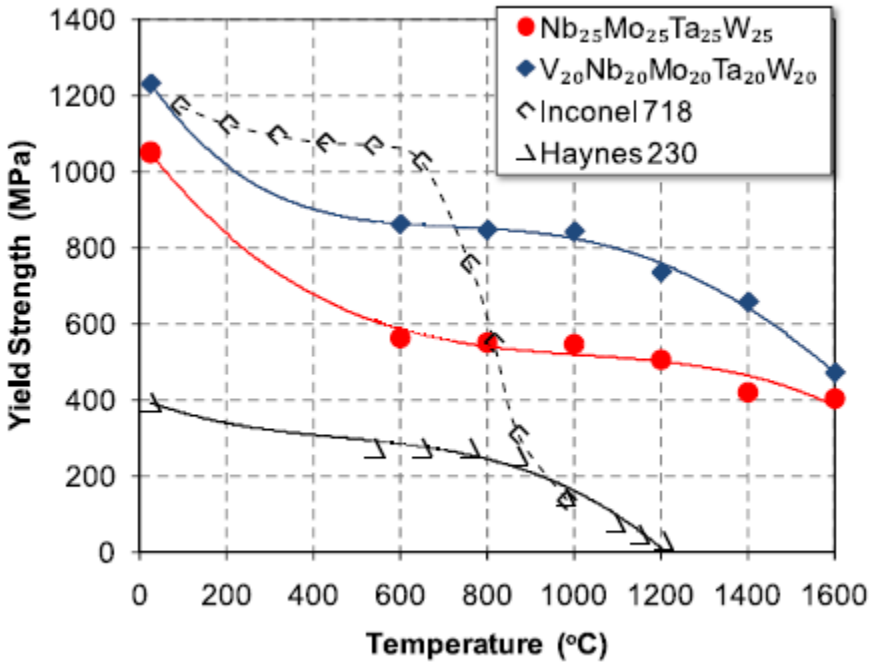
High Entropy Alloys for Fossil Energy Applications

Because of the complex mixing and interactions of atoms, the substitutional diffusion in high-entropy alloys is slow.

The slow diffusion at high temperatures can result in:

- Higher phase stability
- Good creep strength
- Slower oxidation kinetics

Mechanical Properties at High Temperatures



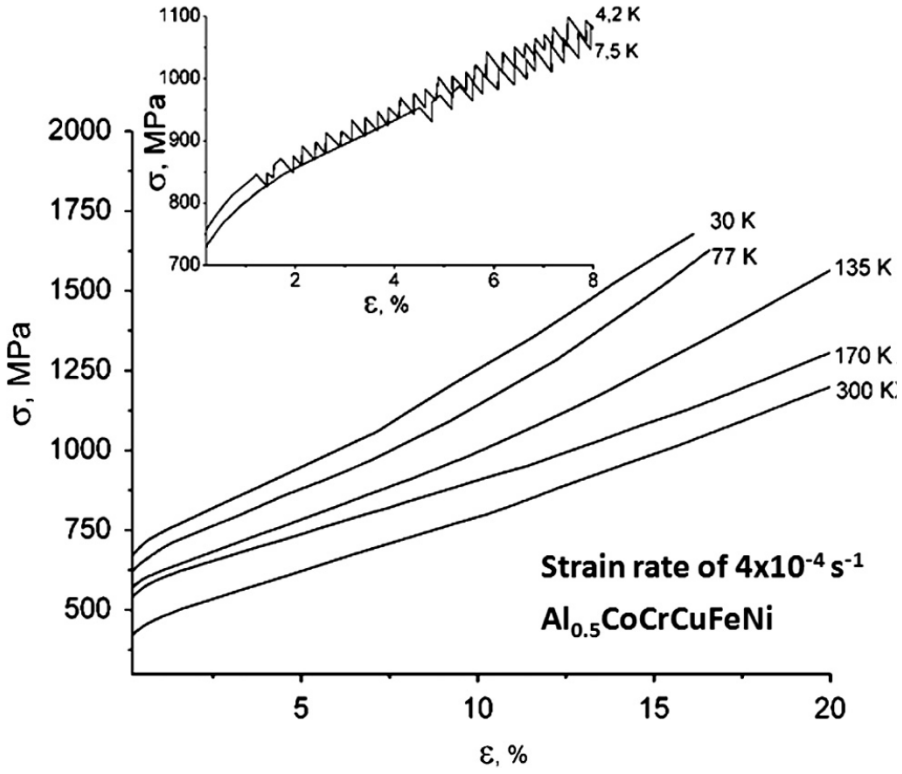
O.N. Senkov et al., Intermetallics, 19 (2011) 698-706.

Challenges in High Entropy Alloy Development

- **Shift in design paradigm leads to vast alloy design space**
- **We need a means by which to pick most promising candidate alloys**
  - Rapid throughput techniques (Miracle *et al.*)
    - Downsize parameter space
    - Synthesize alloy
    - Rapidly characterize
  - Combination of DFT calculations and CALPHAD Screening (Gao)
  - Entropy enhancement of commercial alloy matrices
    - Utilize existing alloy chemistry
    - Modify existing chemistry to maximize entropy
    - Retain microstructural characteristics within reason

Mechanical Response of HEAs

- **Generally trends dictated by the stable crystal structure**
  - BCC-higher strength/lower ductility at RT
  - FCC-lower strength/higher ductility at RT
- **Serrated Plastic Flow**
  - Exhibited by some HEAs
  - Manifests as stress drops during mechanical testing
  - Temperature dependent
  - Strain rate dependent
  - Generally results in higher strength, lower ductility, surface defects



$Al_{0.5}CoCuCrFeNi$ HEA Compression Test at various temperature
Y. Zhang et al. / Progress in Materials Science 61 (2014) 1–93

Processing and Chemistries

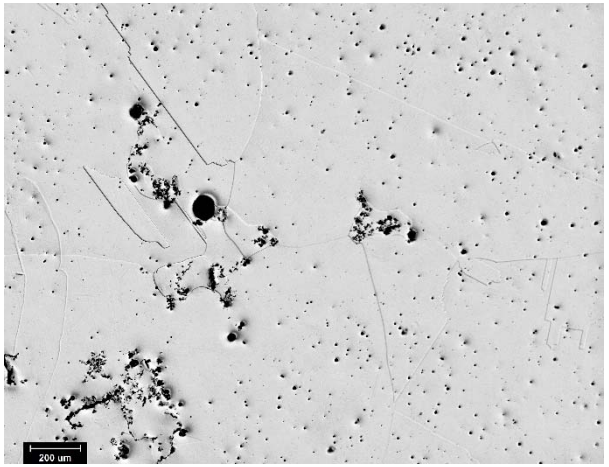
Six alloys were produced using the following methodology.

- Cast using induction melting
- Approximately 160 mm x 75 mm ϕ cylindrical ingots (7 kg)
- Each given computationally optimized homogenization heat treatment
- Thermomechanically processed into ~360 x 127 x 10 mm slabs
- Tensile specimens taken from original ingot bottom
- Tensile tests carried out from room temperature to 800°C
- SEM/TEM carried out on select mechanical test samples

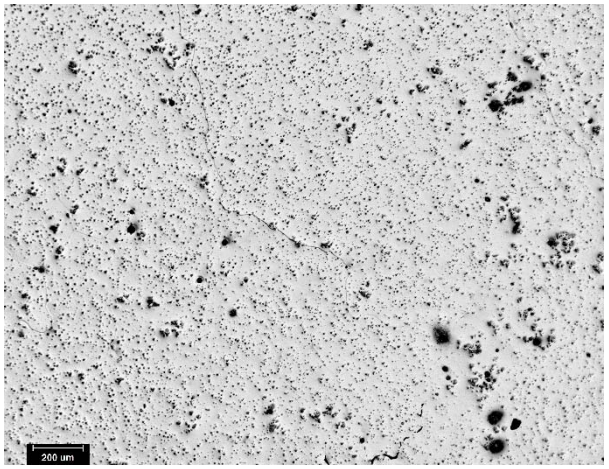
Actual Compositions of alloys (wt%)

ID Name	Ni	Fe	Cr	Co	Mn	Al	Ti	Si	C	Ta
HEASA1	32.82	8.87	20	25.41	7.85	2.03	3.00	0.03	-	-
HEASA2	36.57	14.13	20.24	15.06	7.98	1.87	3.27	0.02	0.25	0.36
HEASA3	41.49	-	18.64	24.94	9.83	1.95	2.81	0.02	-	-
CoCrFeNi	25.9	24.9	22.7	26.0	-	-	-	-	-	-
CoCrFeMnNi	21.5	17.4	19.1	21.7	20.3	-	-	-	-	-
CoFeMnNi	26.1	22.6	-	26.8	24.5	-	-	-	-	-

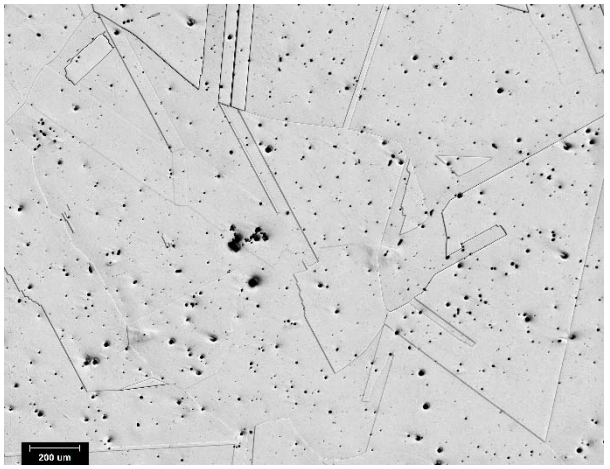
Example As-Cast Microstructural Results



HEASA1-As Cast/Homogenized



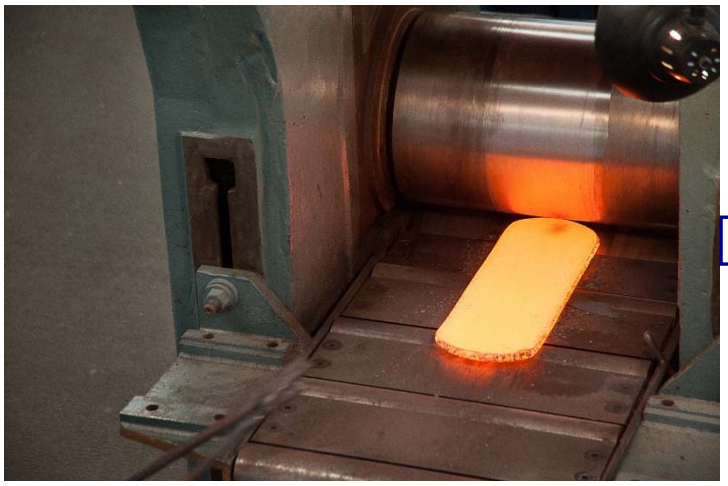
HEASA2-As Cast/Homogenized



HEASA3-As Cast/Homogenized

Forging Operations

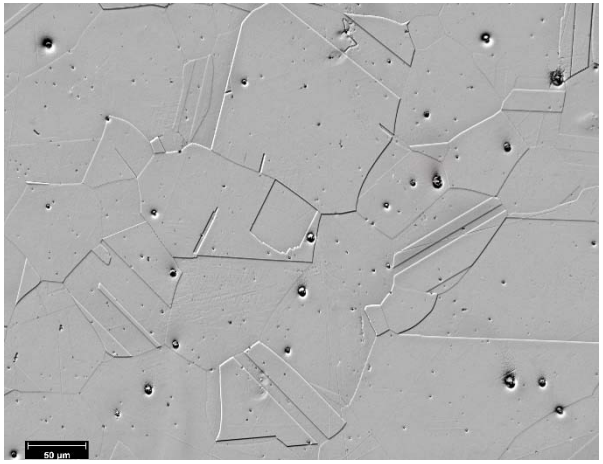
Rolling Operations



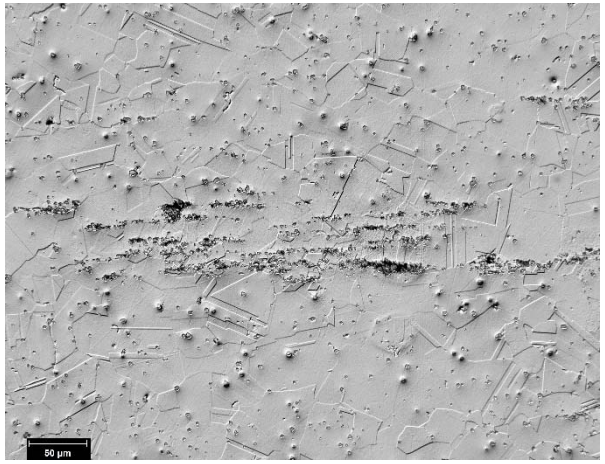
≈ 10 mm thick plate used for tensile specimens

Example Rolled Microstructures

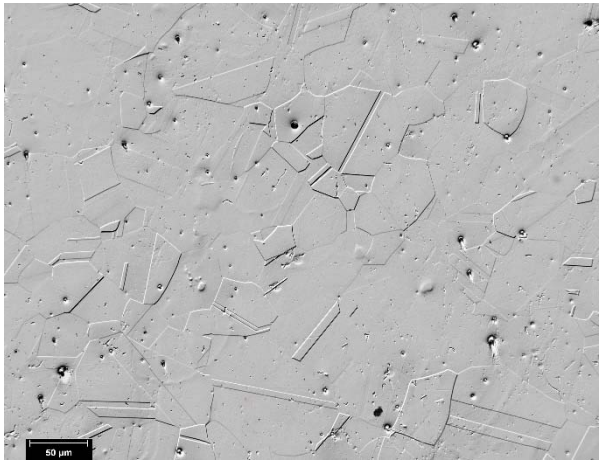
HEASA1



HEASA2

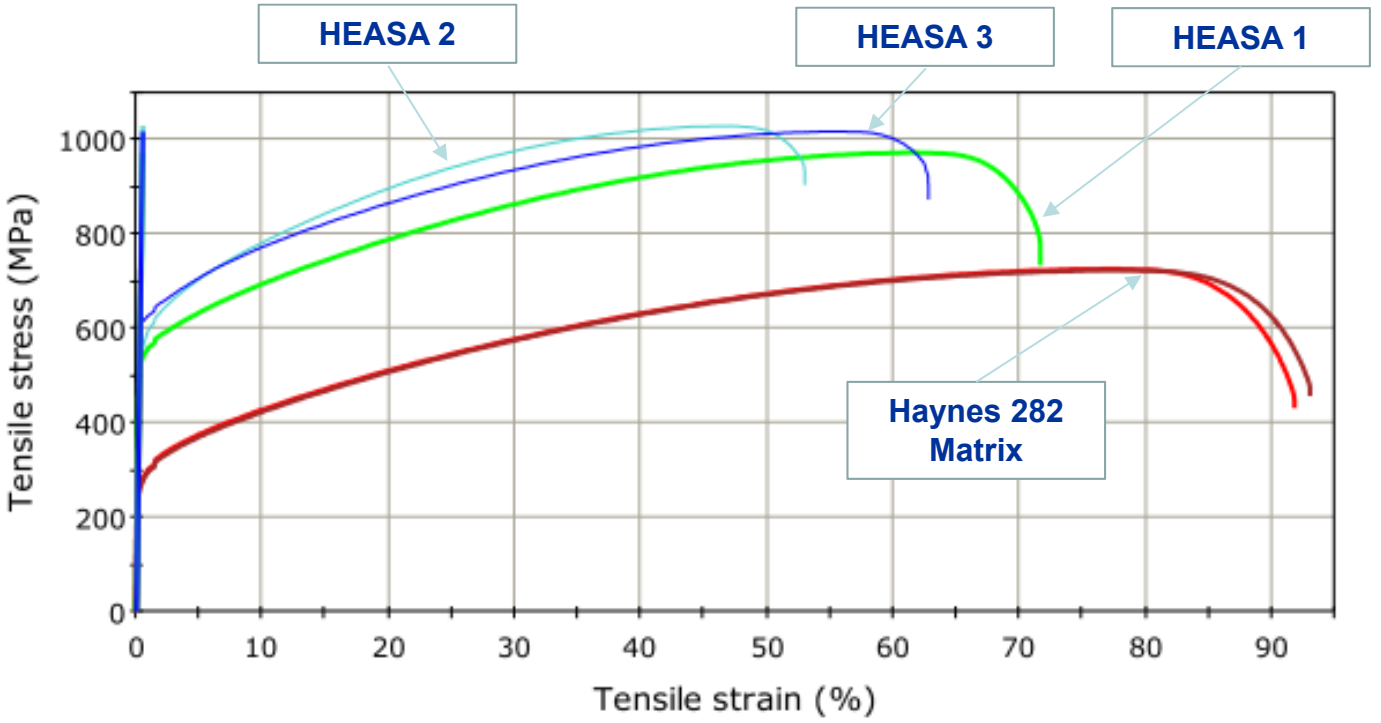


HEASA2



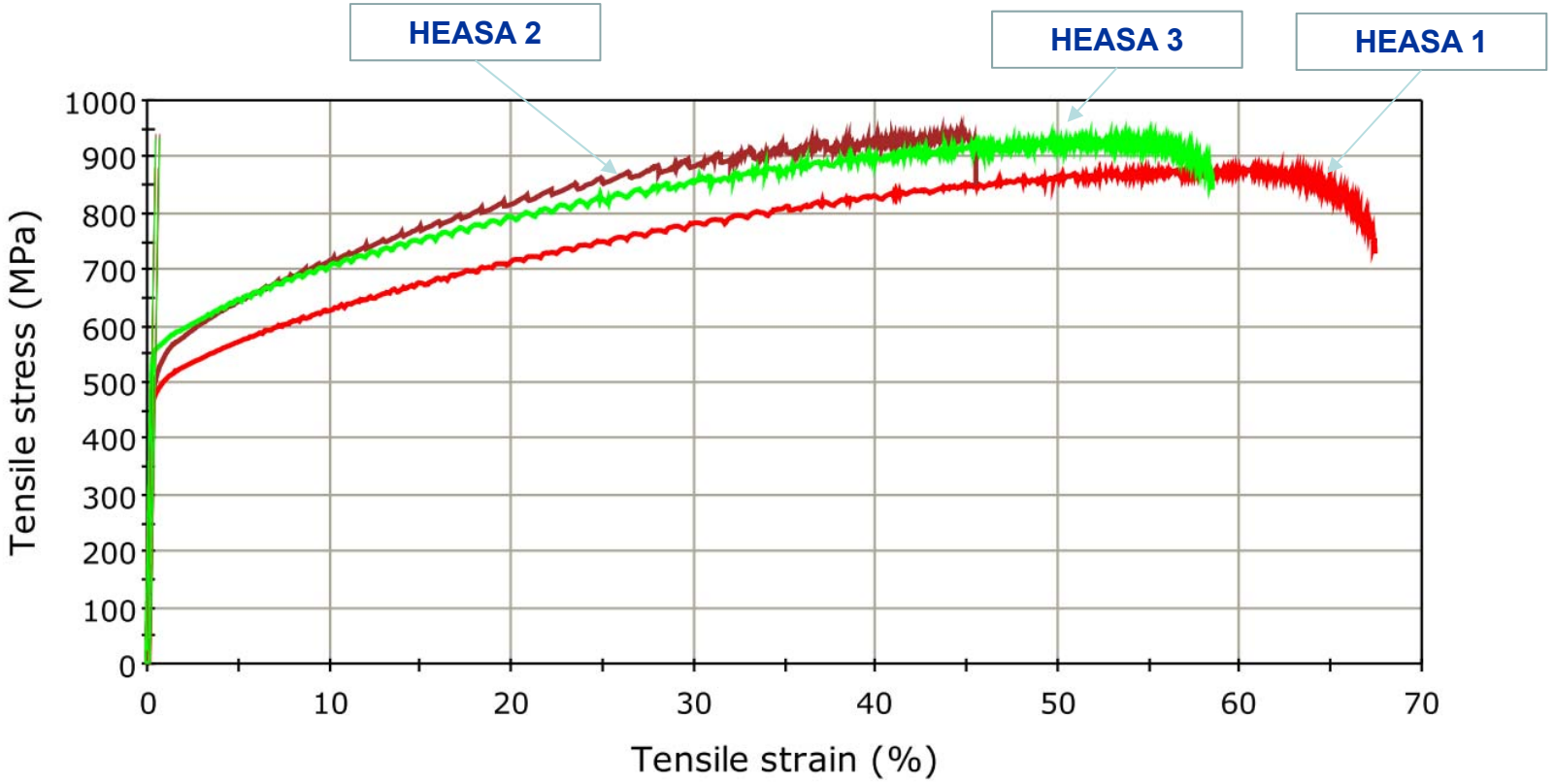
At this magnification, rolled microstructures appeared as expected from CALPHAD predictions, with the exception of linear indications of titanium nitrides. Grain sizes were approximately 50-100 µm in HEASA1,3 and 25-50 µm in HEASA2.

Room Temperature Mechanical Behavior



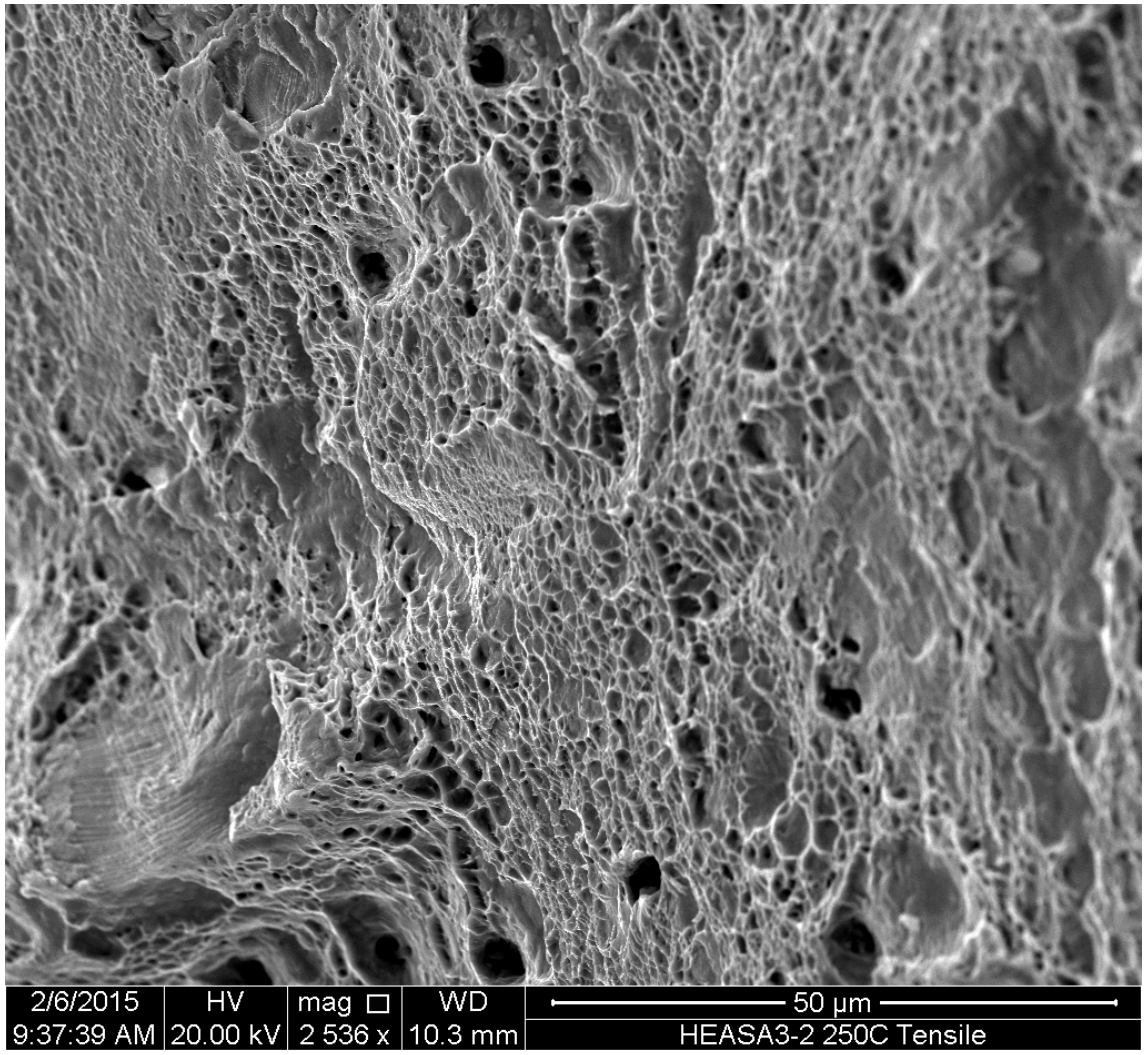
Room temperature behavior exhibited ductile failure with moderate work hardening. No significant anomalies were detected on fracture surfaces examined under SEM.

Elevated Temperature Performance (250°C)



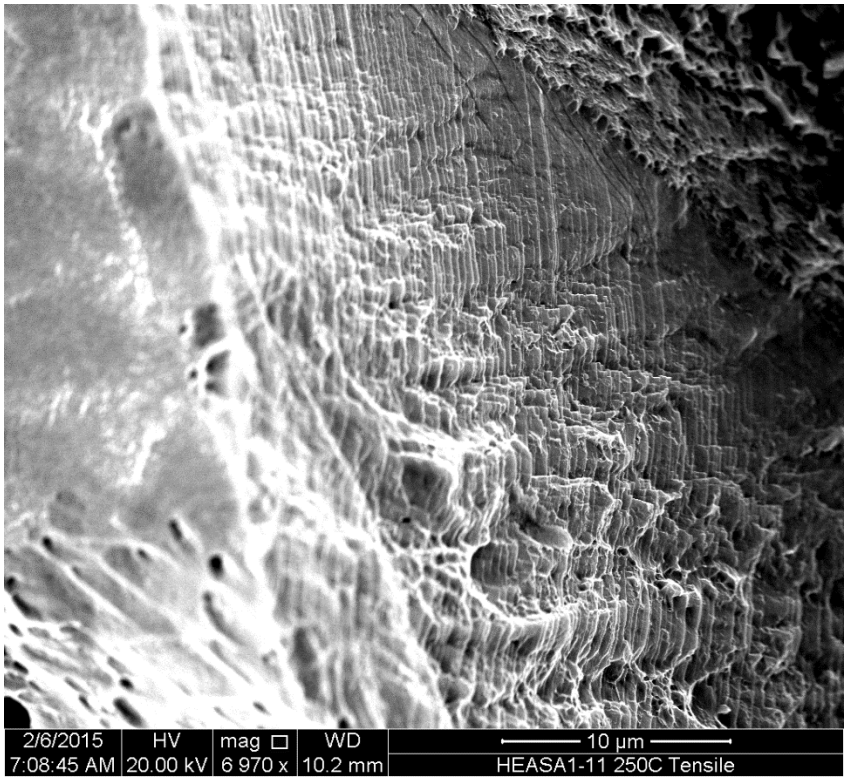
Above 250°C "jerky"/serrated flow was observed after yield accompanied by a repetitive knocking noise. This could be indicative of the Portevin Le Chatelier effect or twinning.

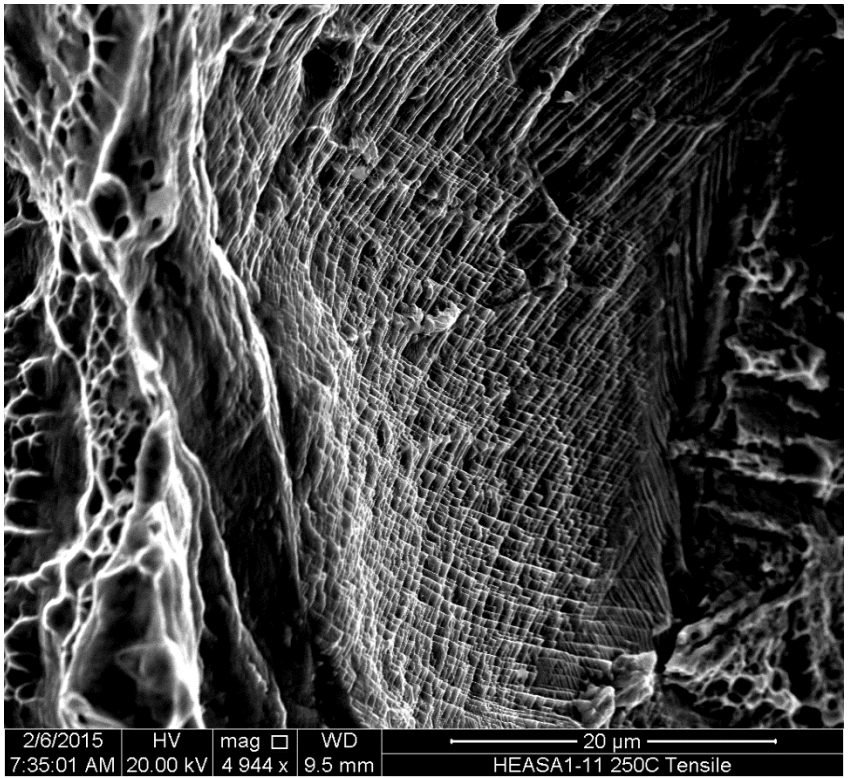
Representative Fracture Surface (SEM)



Fracture in all three specimens was ductile in nature at this temperature with several “ledged” regions becoming apparent upon closer examination.

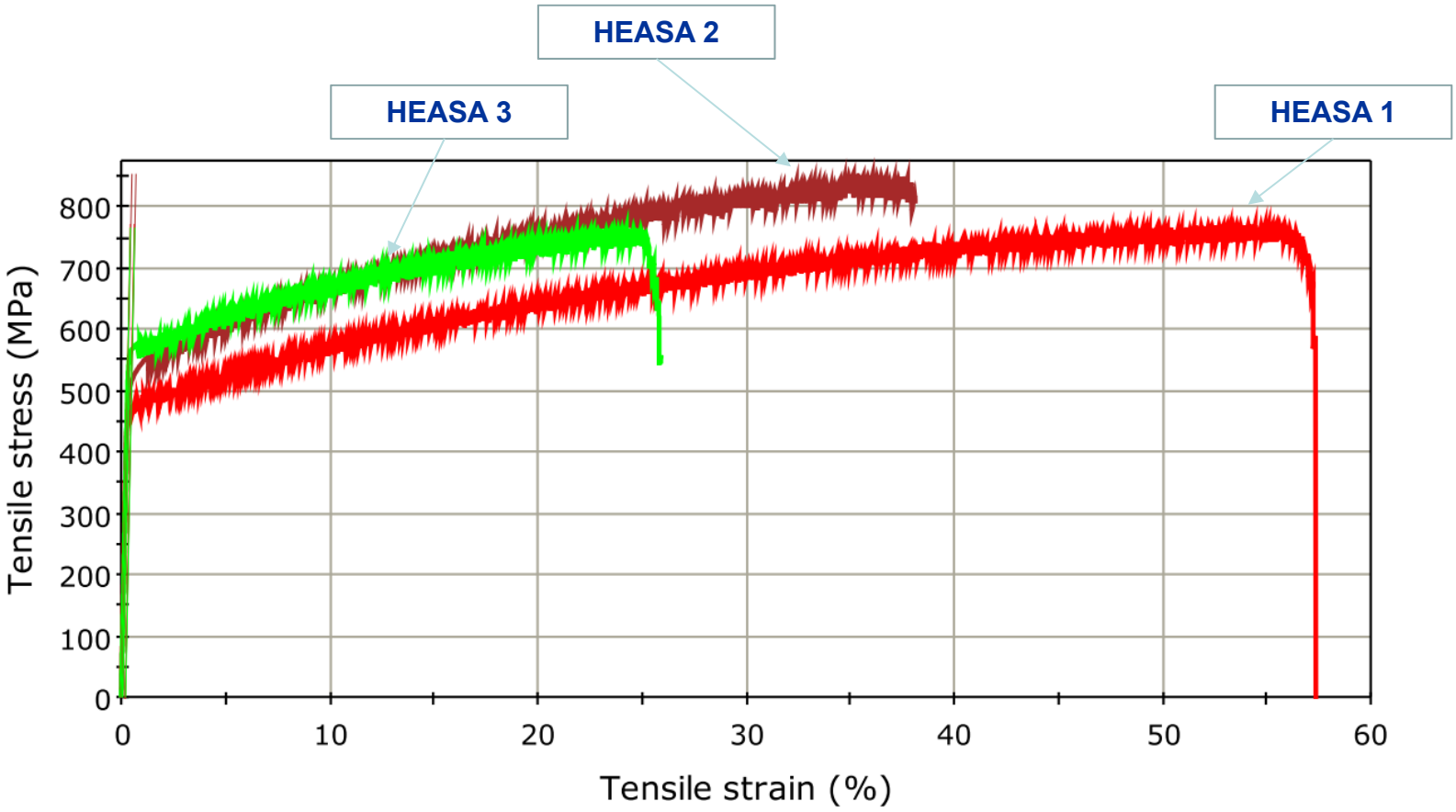
SEM of Striations on Fracture Surface





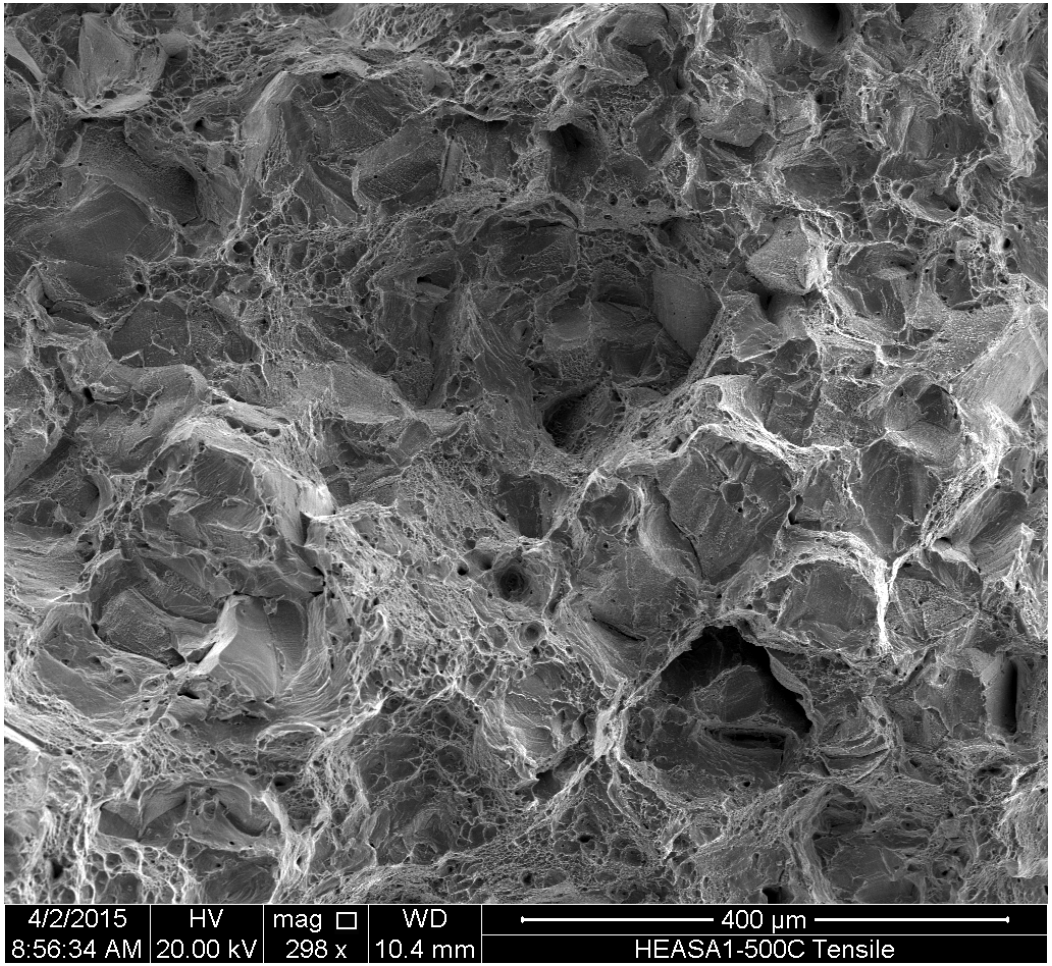
Ledged fracture surfaces appeared very frequently in all three alloys. The orientation of the ledged surfaces was approximately 45-55° relative to the tensile axis. The orientation of the ledged surfaces matches similar features observed when the Portevin Le Chatelier effect becomes active.

Elevated Temperature Tensile Tests 500°C



All three alloys again exhibited jerky flow at 500°C at a much higher frequency and with greater stress drop magnitude. Ductility was also decreased significantly with the exception of HEASA1.

Representative Fracture Surface (SEM)

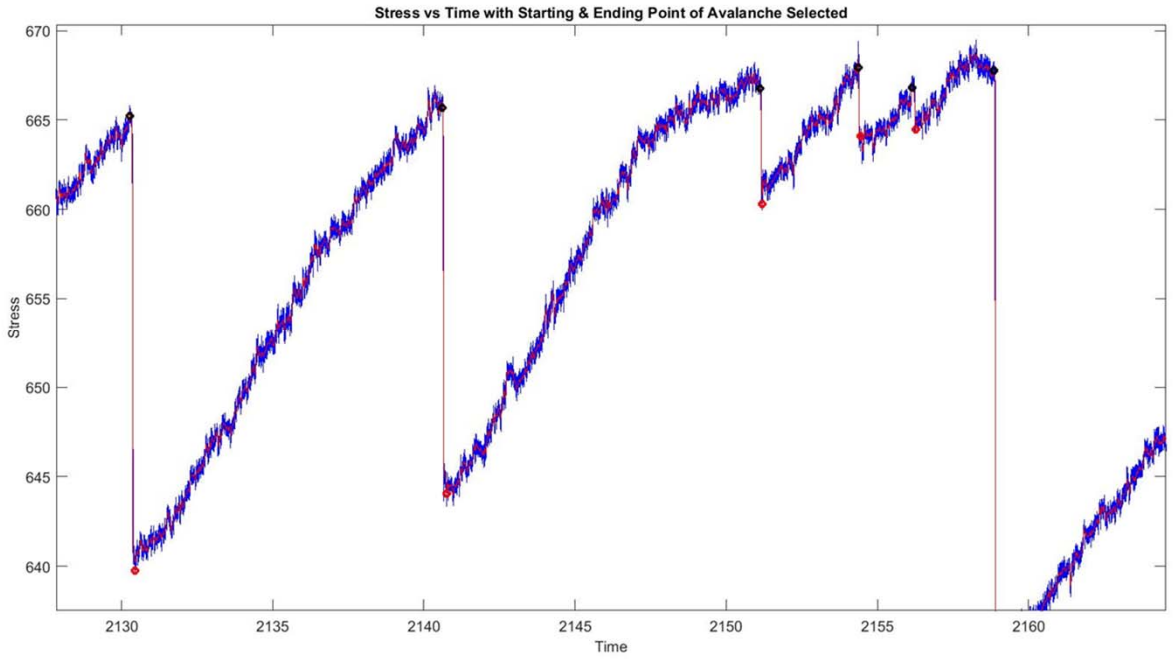


Fracture surfaces in all three alloys exhibited a mixed mode of failure including intergranular, transgranular, and ductile failure.

Complimentary Cumulative Distribution Function Analysis

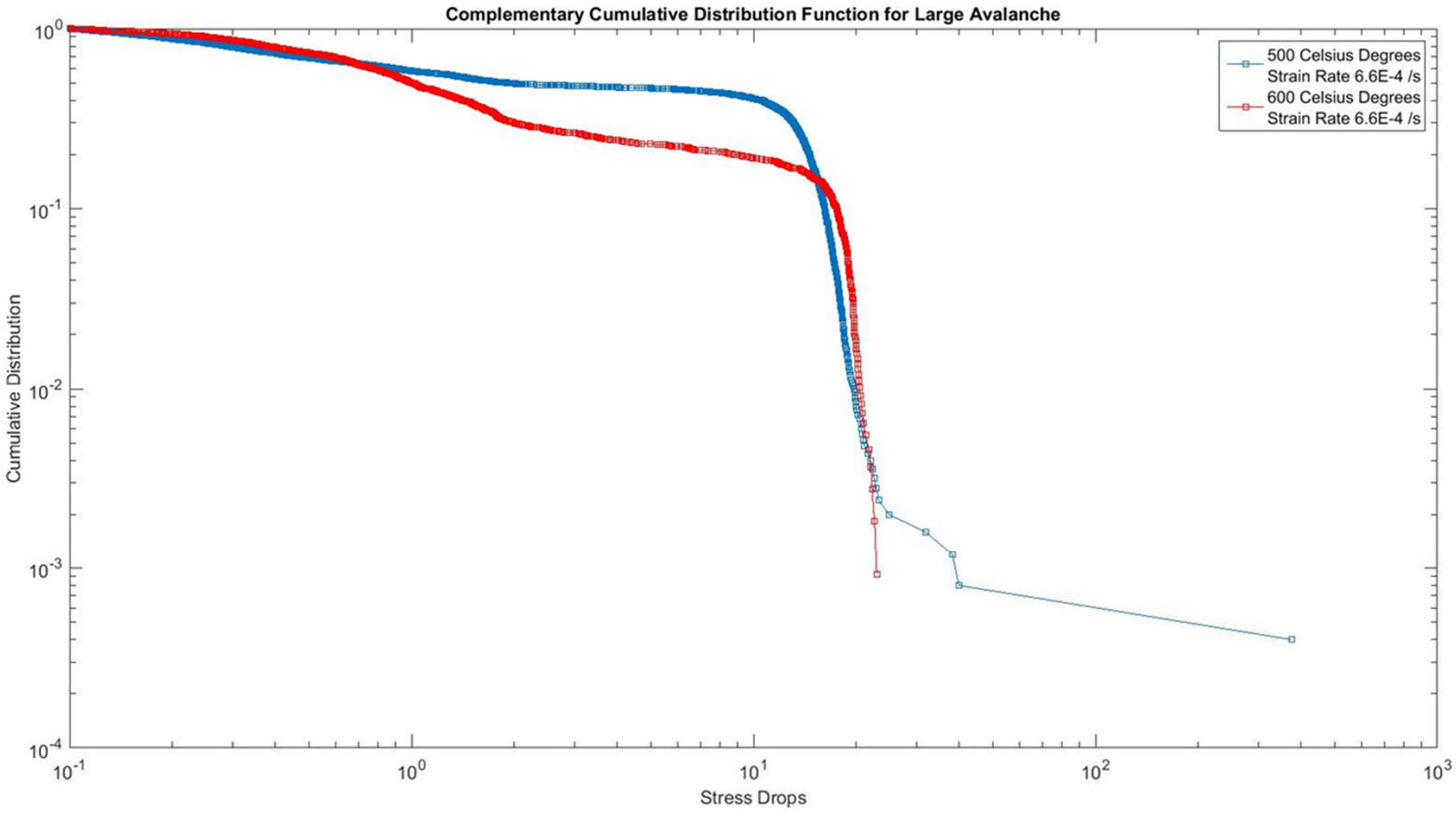
- Utilized by theoreticians to model slip drop behavior in HEA systems as well as bulk metallic classes etc.
- Quantifies the probability of finding slip drops of a given magnitude within the tensile curve
- Model has several tuning parameters that can be used to estimate trends such as temperature, strain rate and other dependencies of serrated flow
- The analysis presented was conducted only on HEASA1 alloys

Result



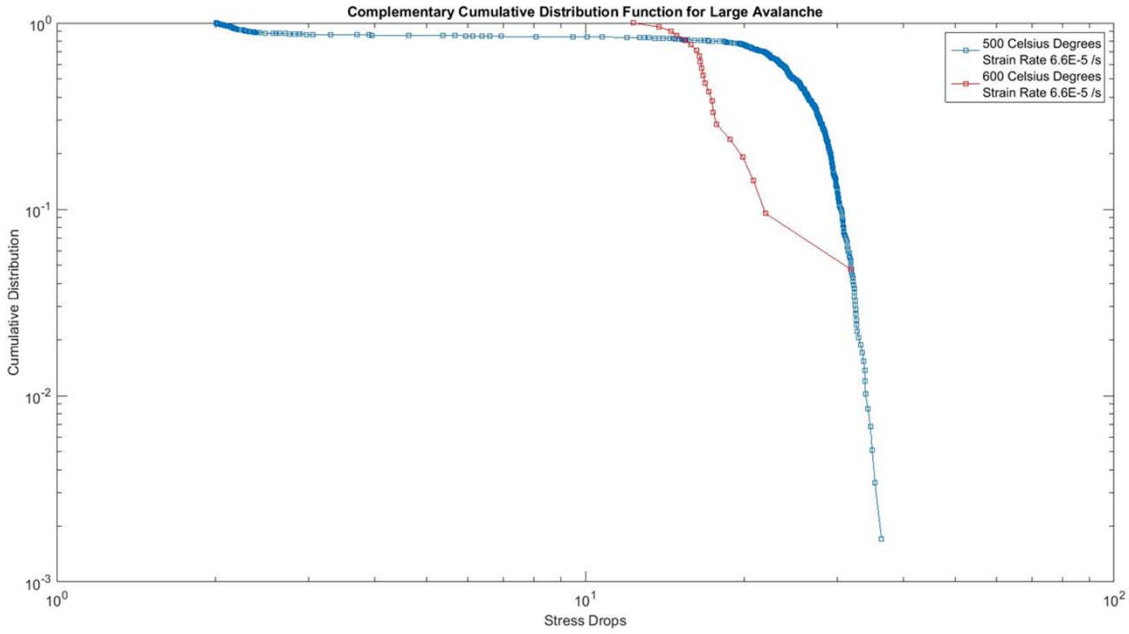
Stress vs Time for Strain Rate 6.6E-5 /s Temperature 500 Celsius Degrees with Marked Black & Red dots representing Beginning & Ending of avalanche

Result in Complementary Cumulative Distribution Function (Temperature Dependence) 6.6E-4 /s



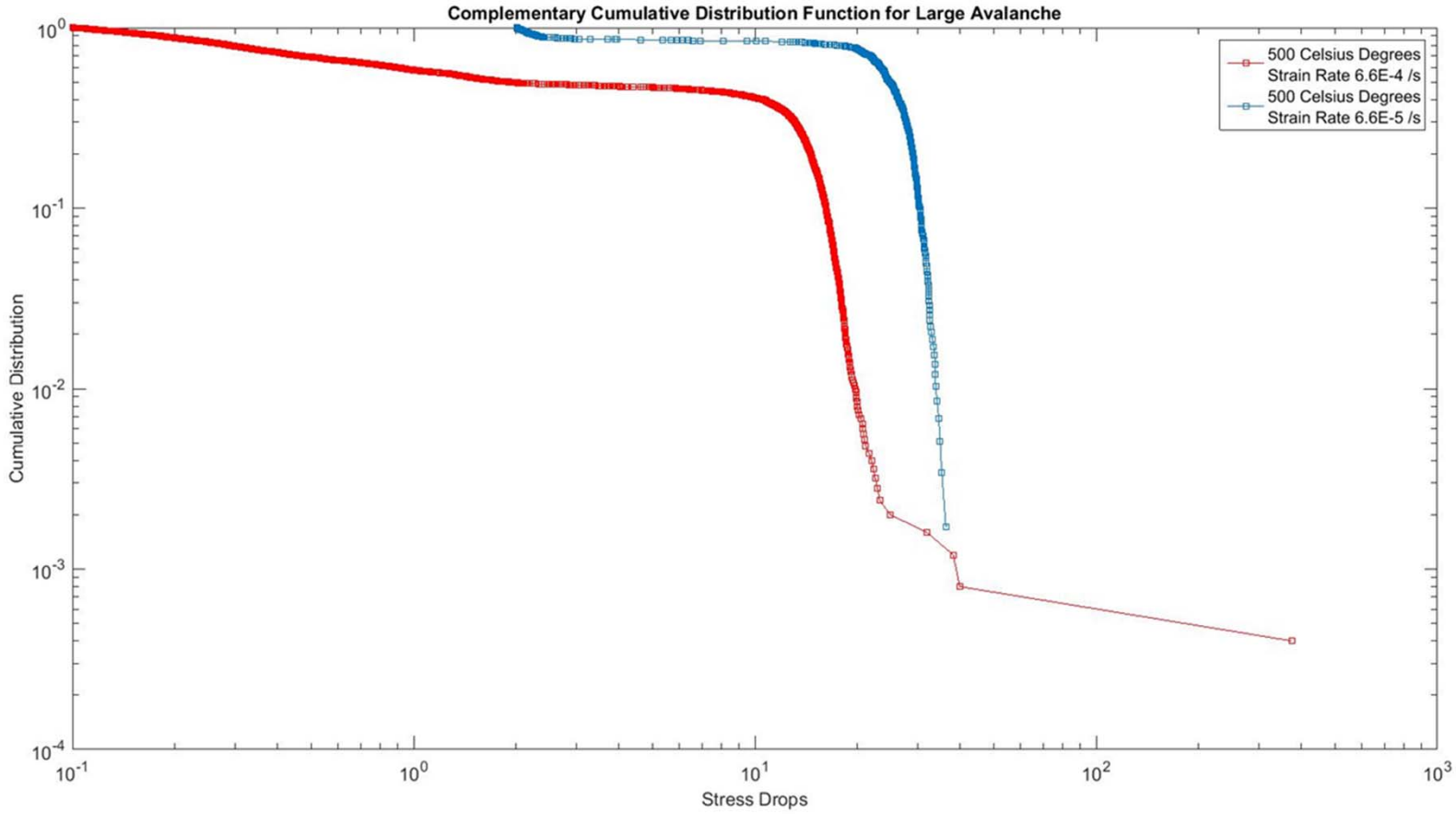
CCDF for Strain Rate 6.6E-4 /s at 500 & 600 Celsius Degrees

Result in Complementary Cumulative Distribution Function (Temperature) Dependence) 6.6E-5 /s



CCDF for Strain Rate 6.6E-5 /s at 500 & 600 Celsius Degrees

Result in Complementary Cumulative Distribution Function (Strain Rate Dependence) 500 C



CCDF for 500 Celsius Degress at Strain Rate 6.6E-4 /s & 6.6E-5 /s

Test Matrix for CoCrFeNi, CoCrFeMnNi, CoFeMnNi

CoCrFeNi, CoCrFeMnNi with residual work, CoFeMnNi

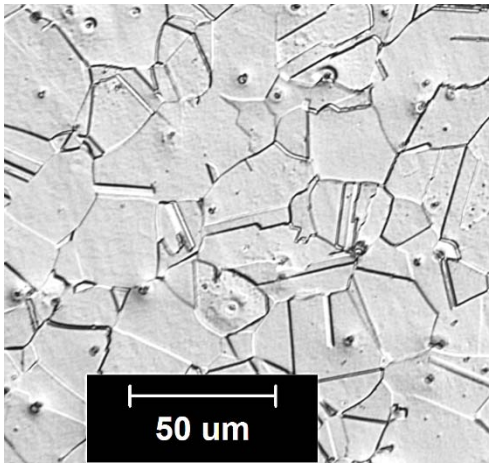
Strain Rates (1/s)	250	500	600	800
6.66e-5, 6.66e-4	X	X	X	X

Constant Strain Rate (CSR), CoCrFeNi, CoCrFeMnNi

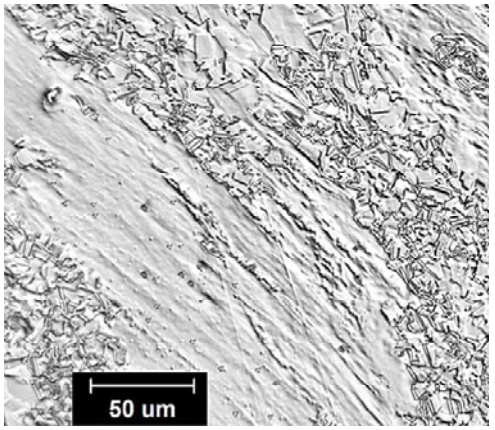
Strain Rate (1/s)	250	500	600	800
6.66e-6 (CSR3)		O	O	
6.66e-5 (CSR2)	O	O	O	O
6.66e-4 (CSR1)	O	X	X	O

Rolled HEA Microstructures

- CoCrFeNi, CoCrFeMnNi, and CoFeMnNi alloys appear to be *essentially* single phase.
- Original CoCrFeNi and CoCrFeMnNi grain size <10 μm, with some residual wrought structure
- Additional CoCrFeNi, and CoCrFeMnNi samples were also created with limited residual work
- Grain size ~10-25 μm for CoFeMnNi
- A small volume fraction of S- and Mn-rich precipitates or inclusions were found in CoCrFeNi and CoCrFeMnNi alloys.
- All materials contain the occasional unexpected inclusion (silica/alumina).

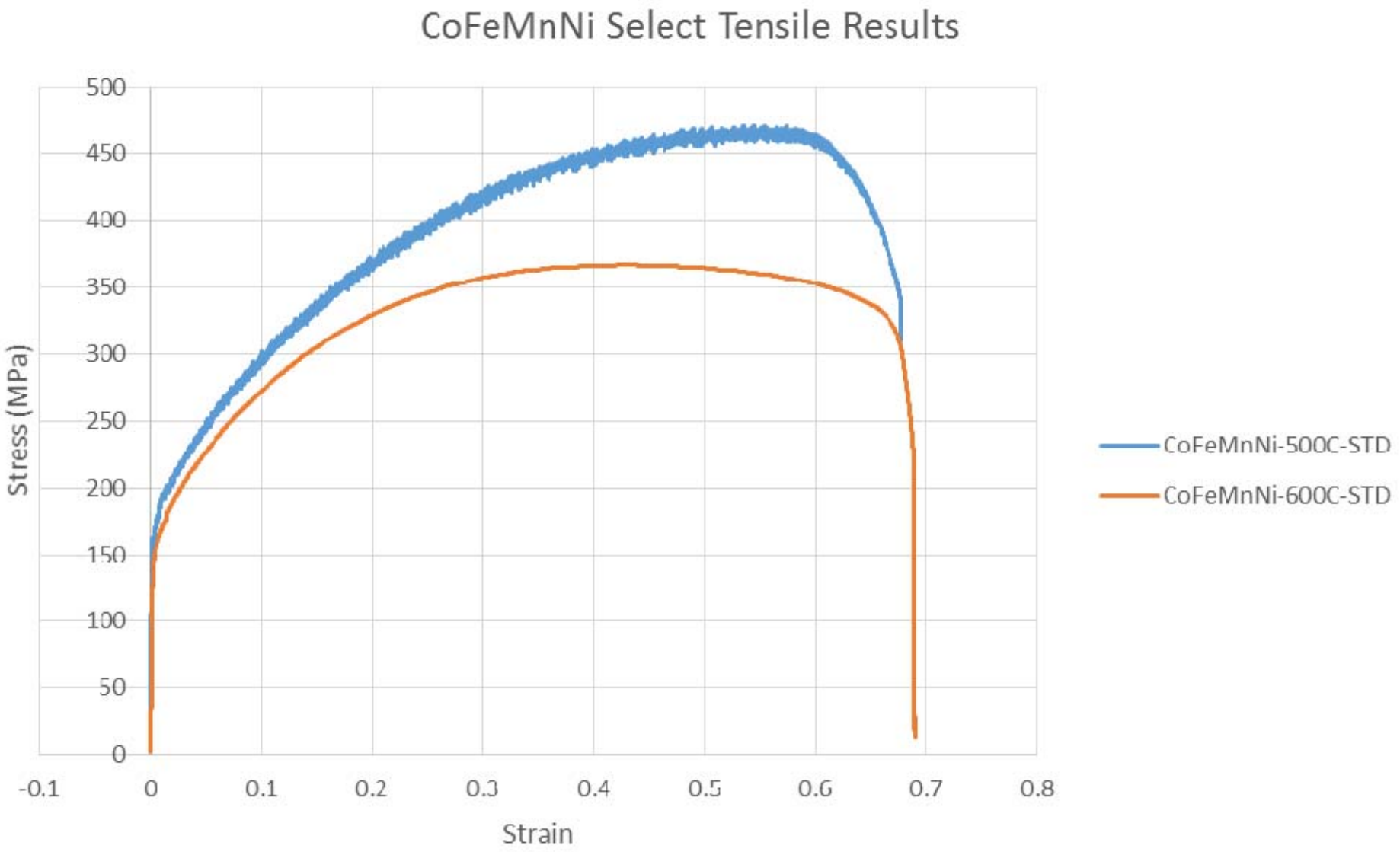


Optical micrograph of CoFeMnNi after rolling operations.

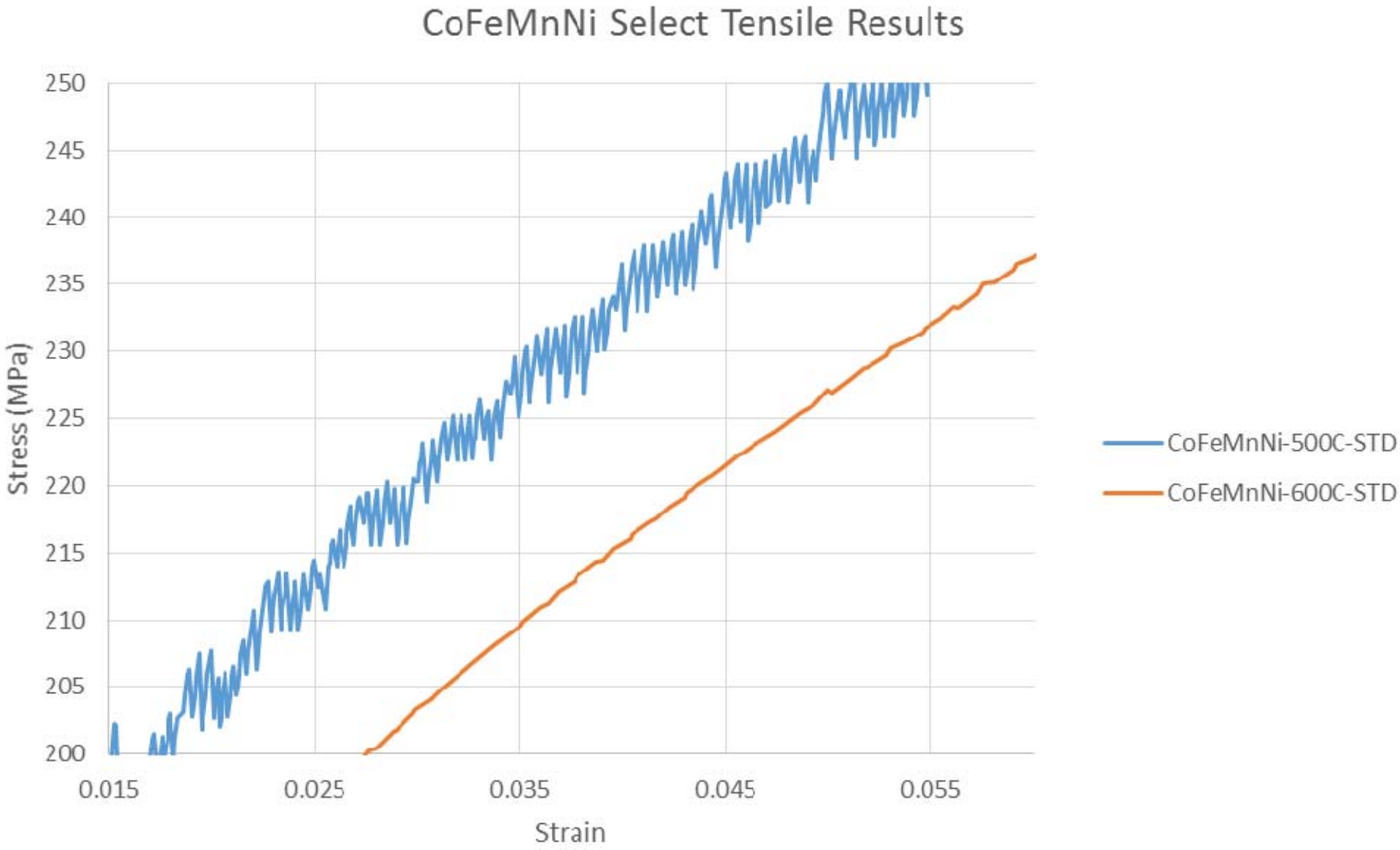


Optical micrograph of CoCrFeMnNi after rolling operations revealing residual wrought structure.

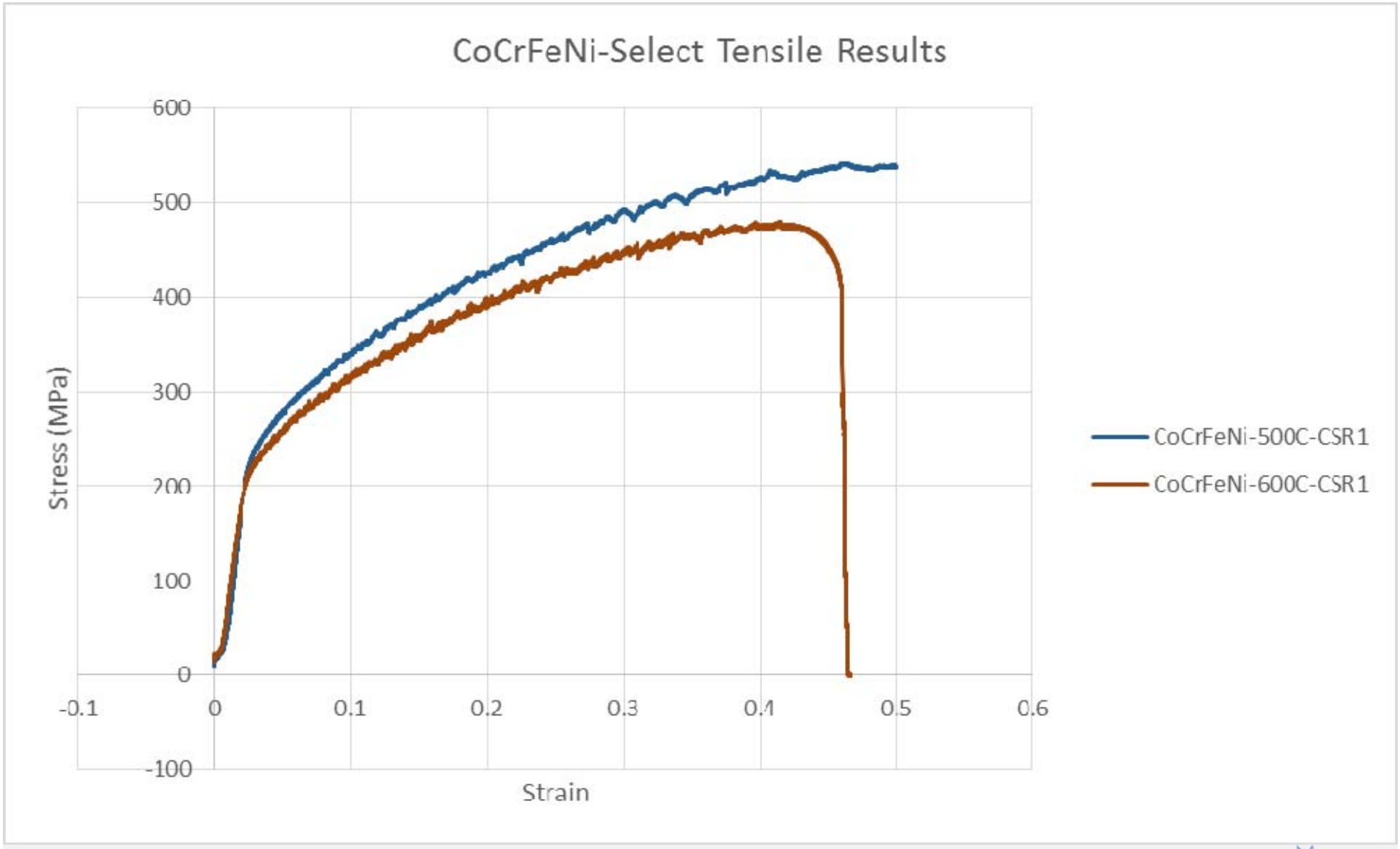
Temperature Effects (CoFeMnNi)



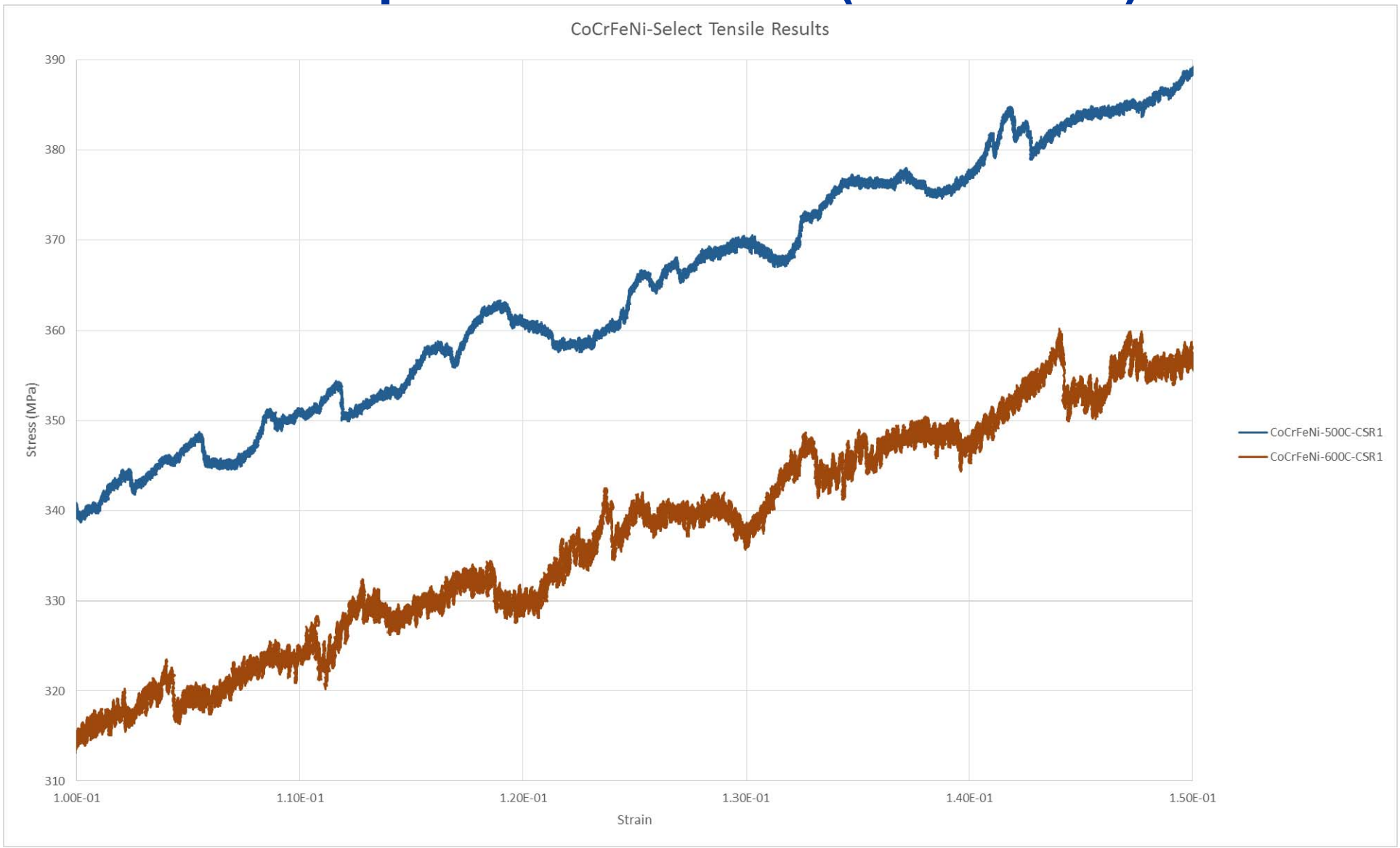
Temperature Effects (CoFeMnNi)



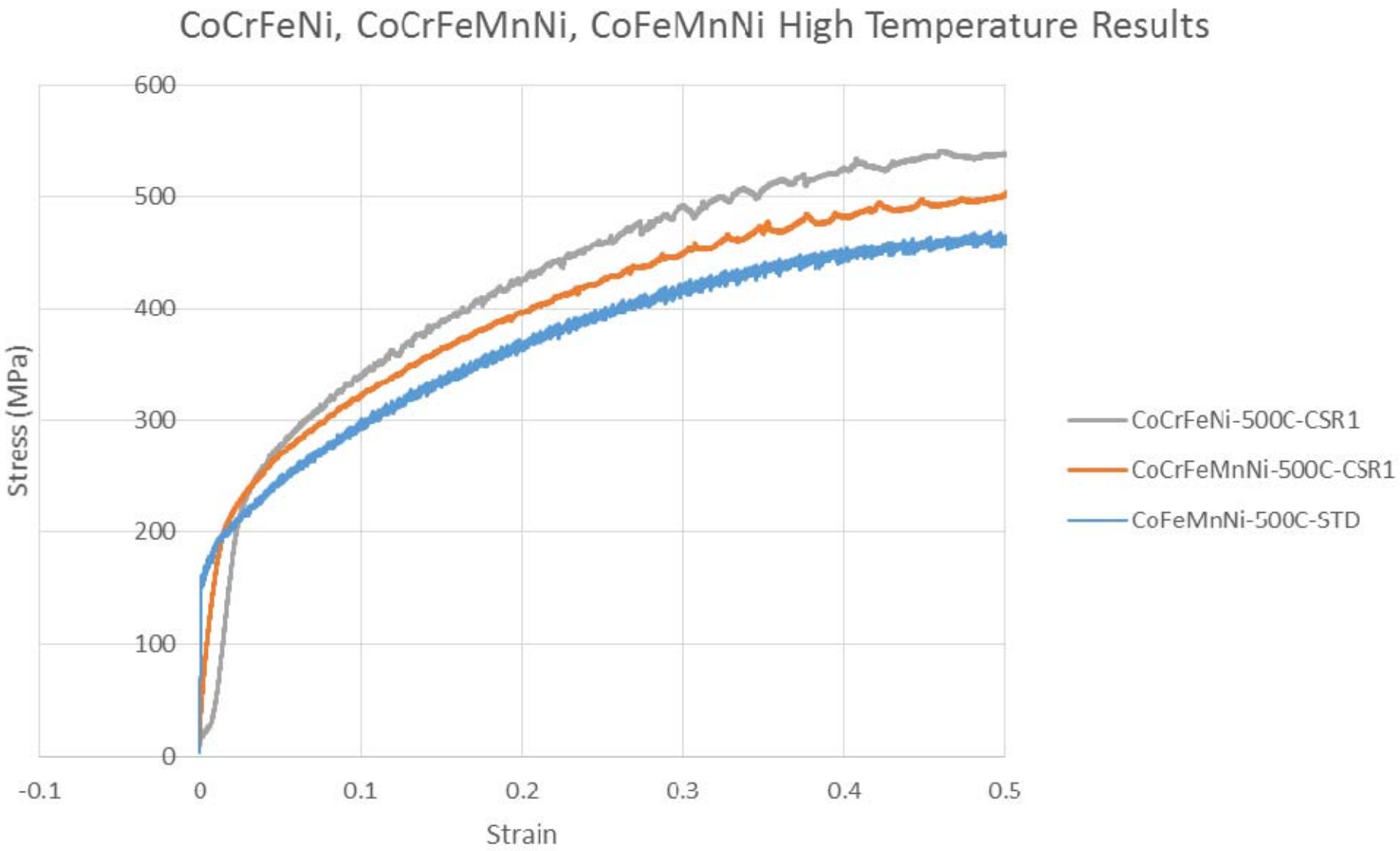
Temperature Effects (CoCrFeNi)



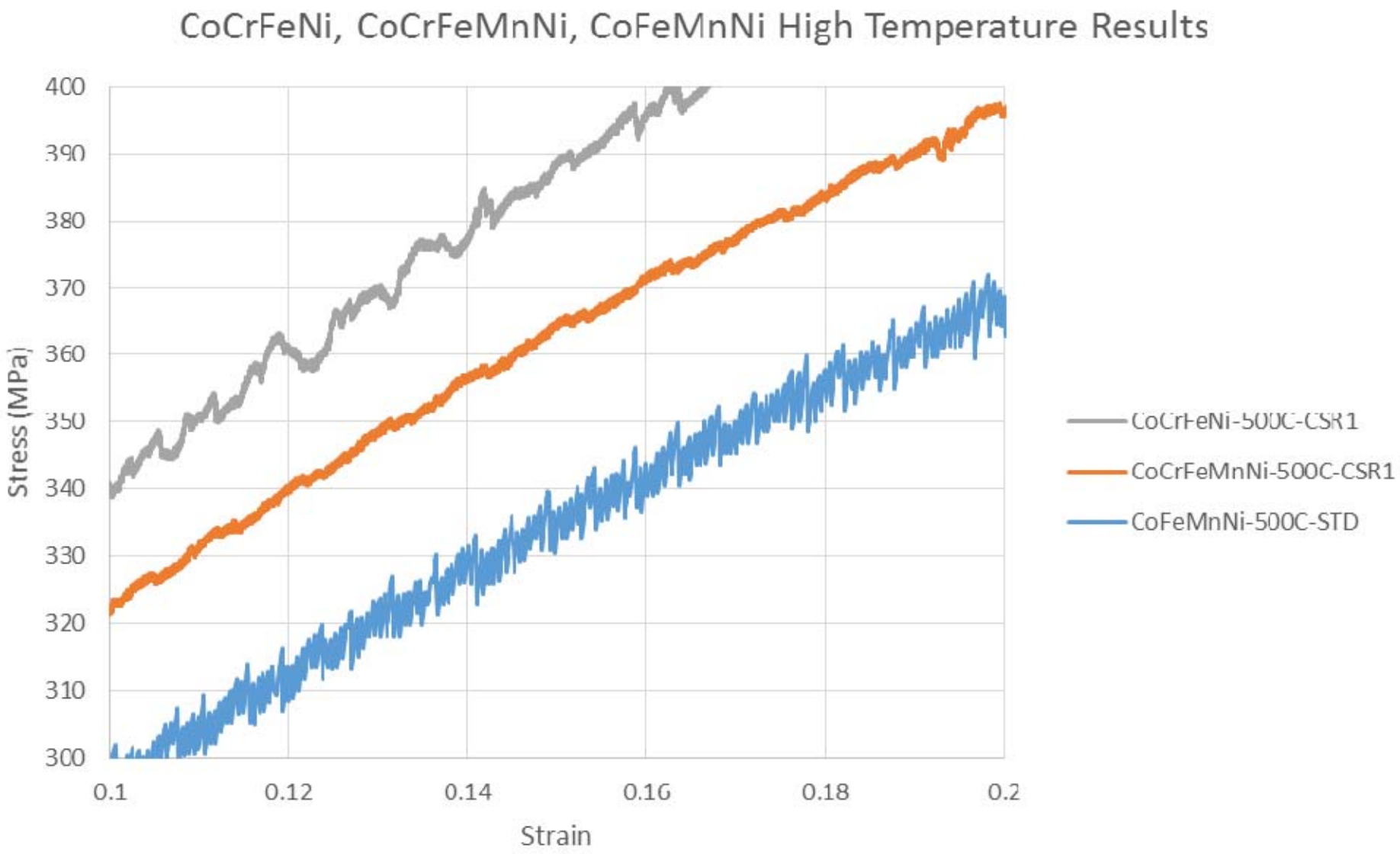
Temperature Effects (CoCrFeNi)



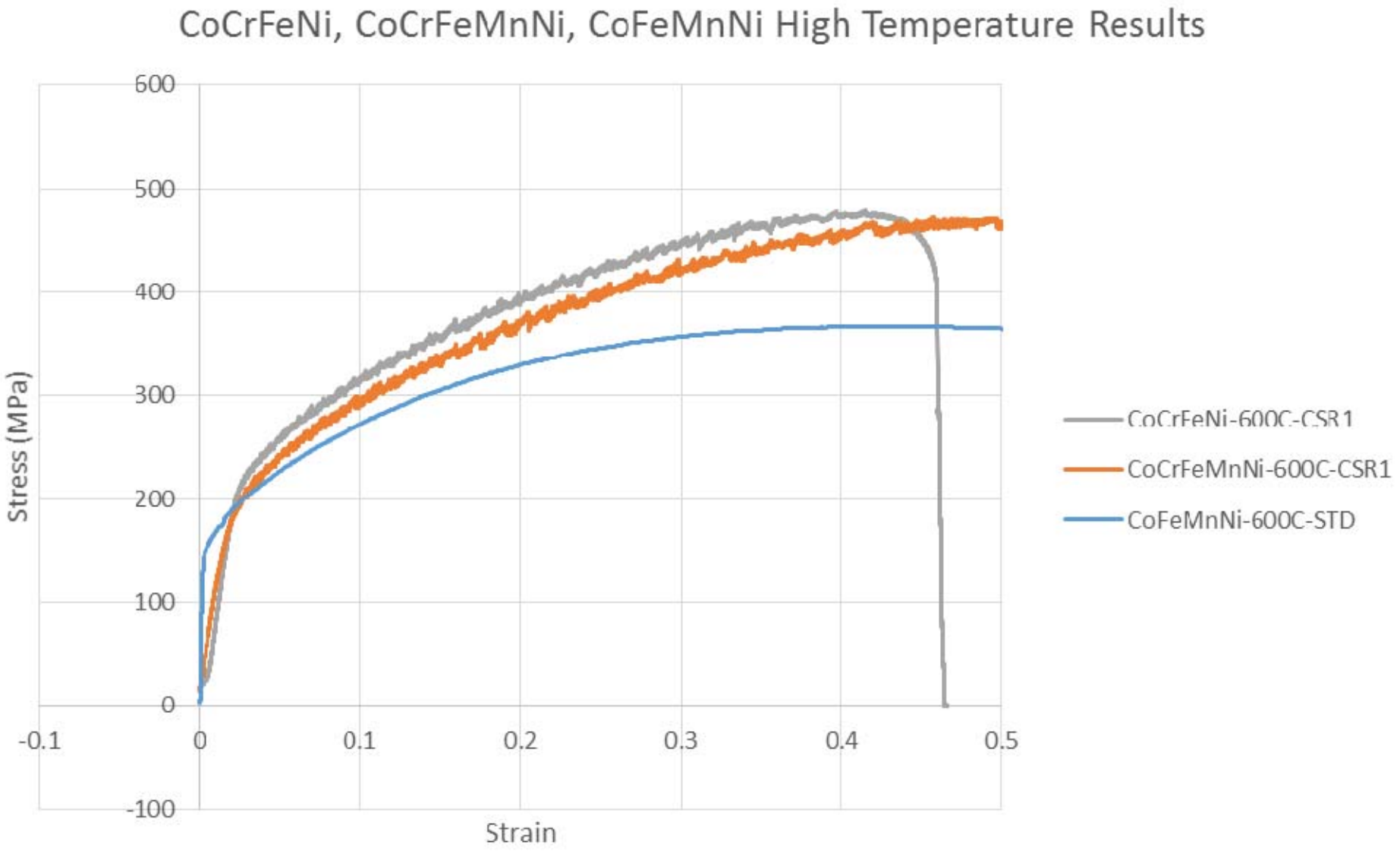
Chemistry Effects (Mn vs. Cr) at 500C



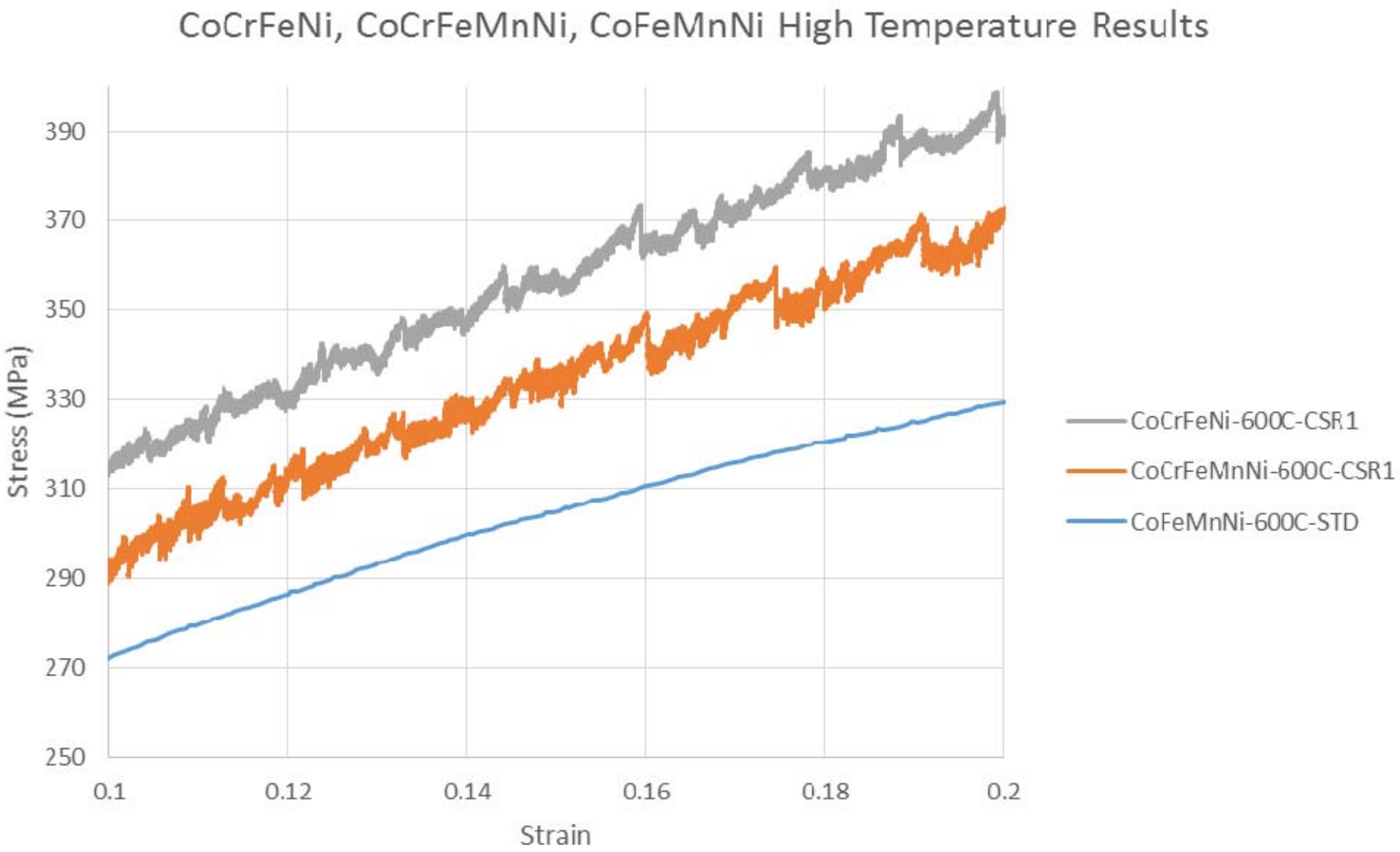
Chemistry Effects (Mn vs. Cr) at 500C



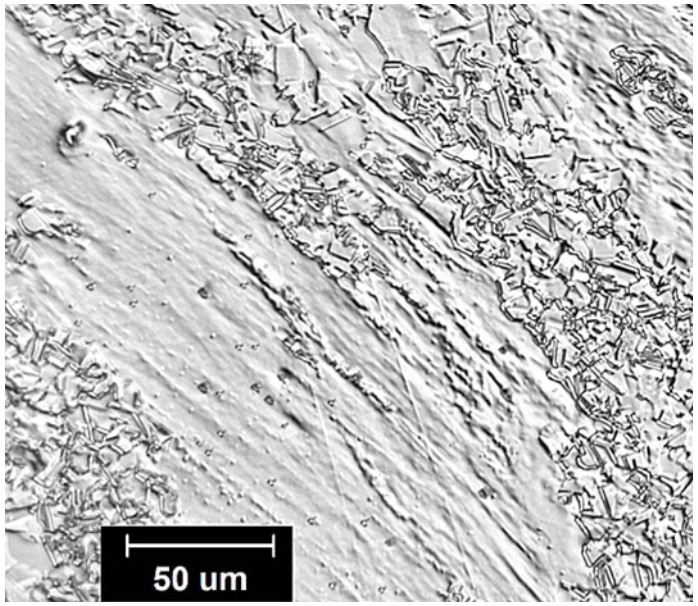
Chemistry Effects (Mn vs. Cr) at 600C



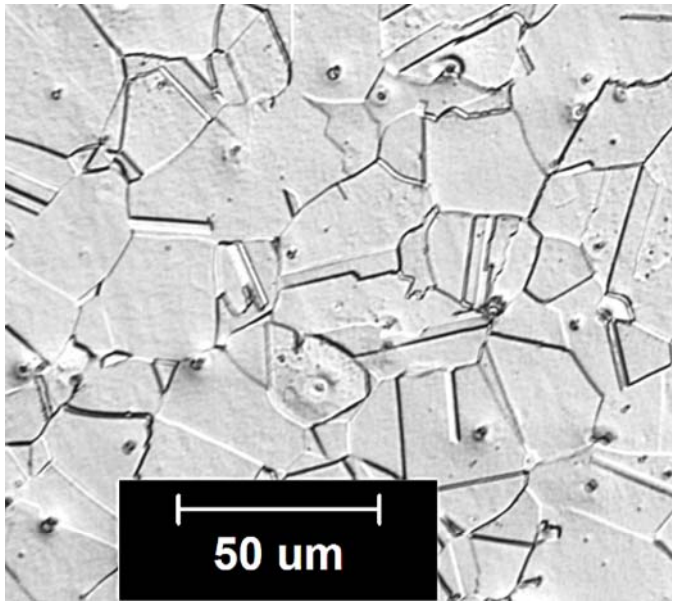
Chemistry Effects (Mn vs. Cr) at 600C



Residual Work Structures

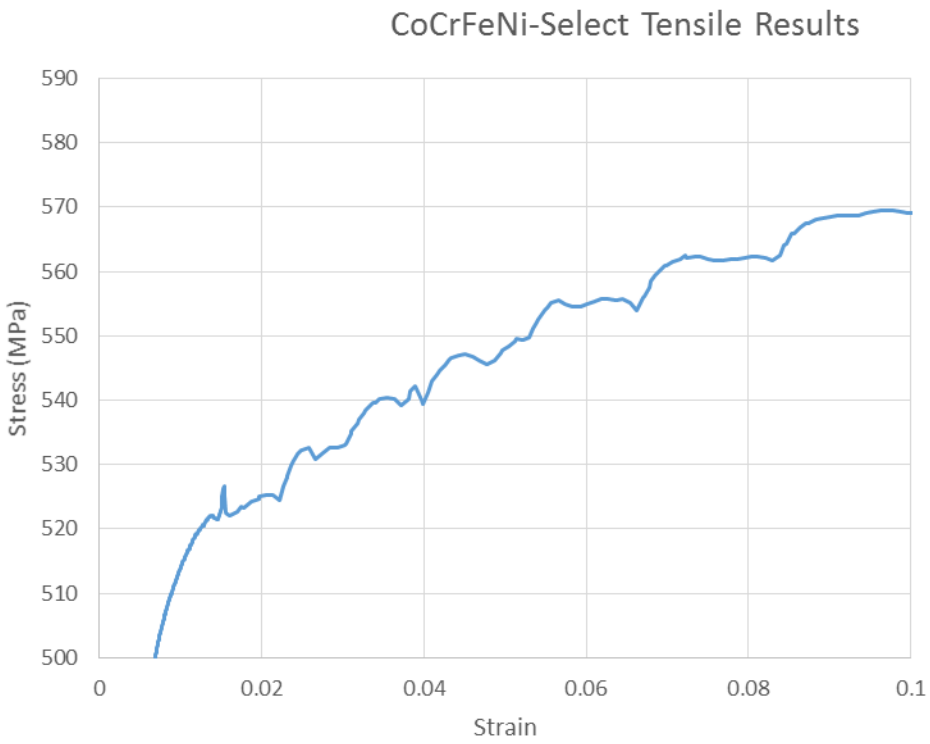


Banded Grain Structure (high residual work)

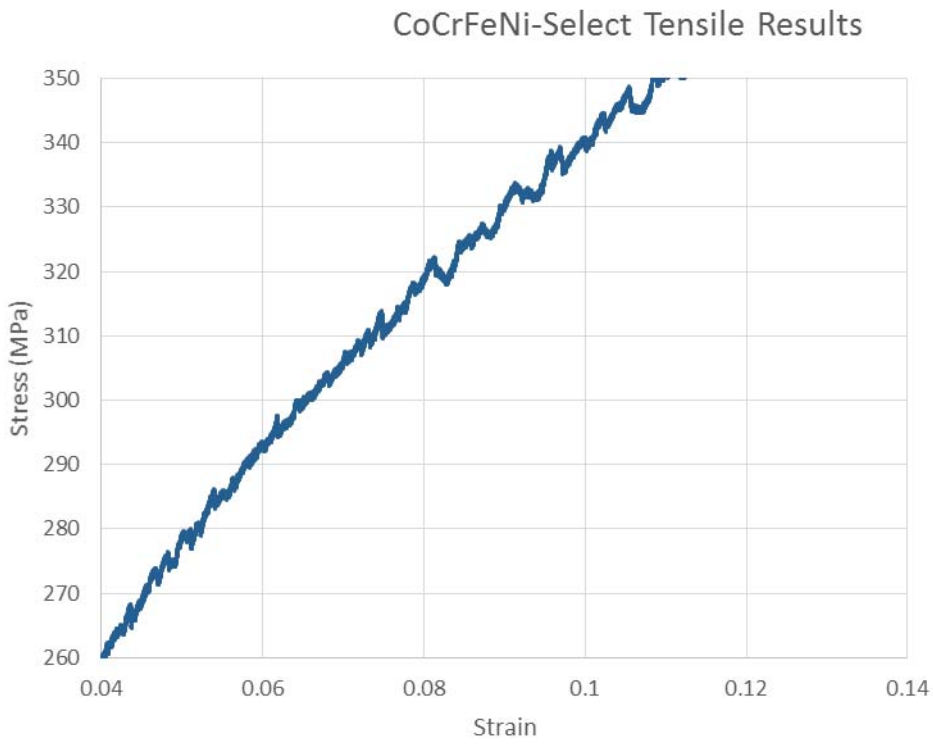


Equiaxed Grain Structure (low residual work)

CoCrFeNi Residual Work Effects 500C

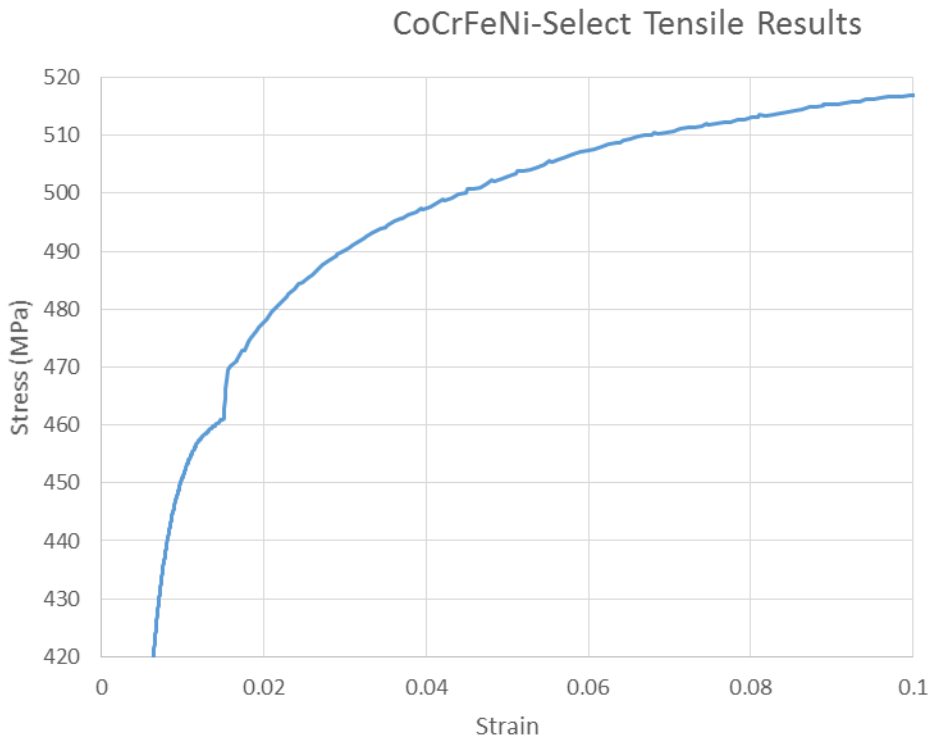


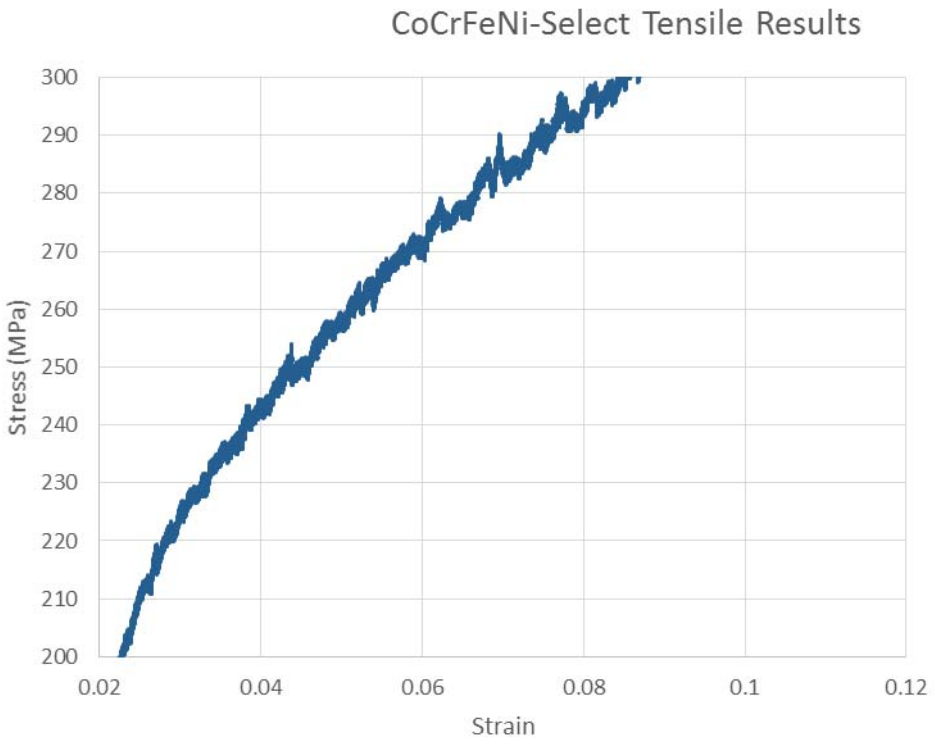
Sample contained residual wrought structure



Sample contained NO residual wrought structure

CoCrFeNi Residual Work Effects 600C

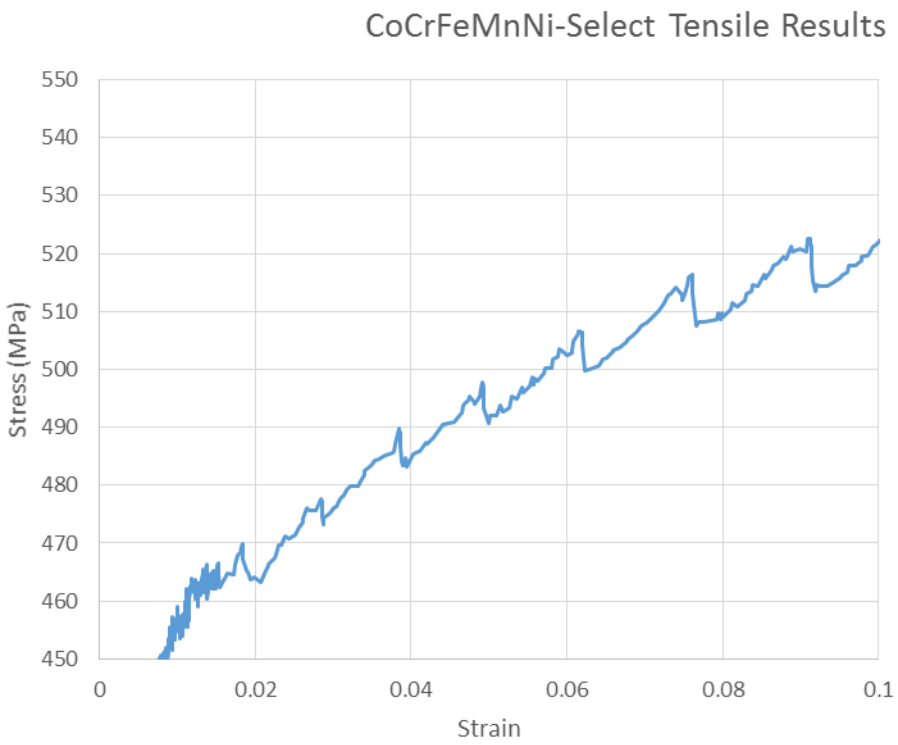




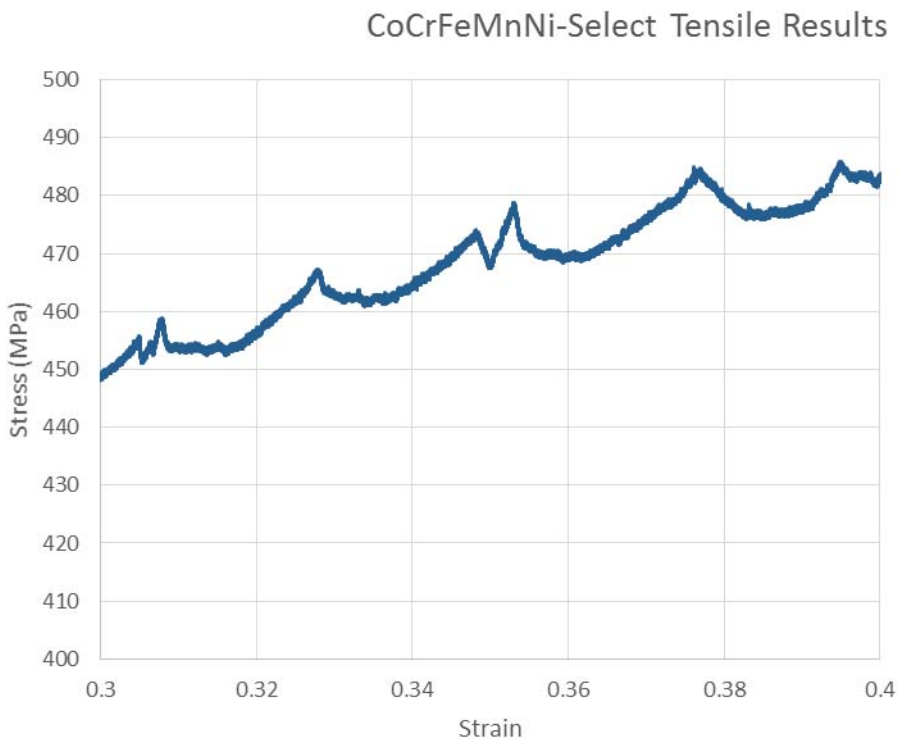
Sample contained residual wrought structure

Sample contained NO residual wrought structure

CoCrFeMnNi Residual Work Effects 500C

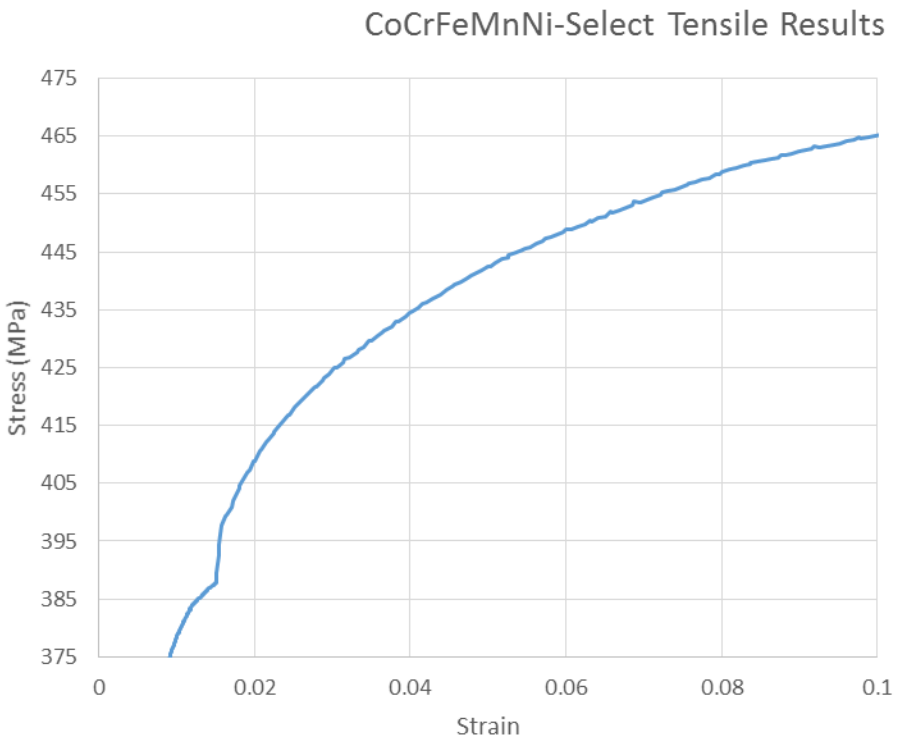


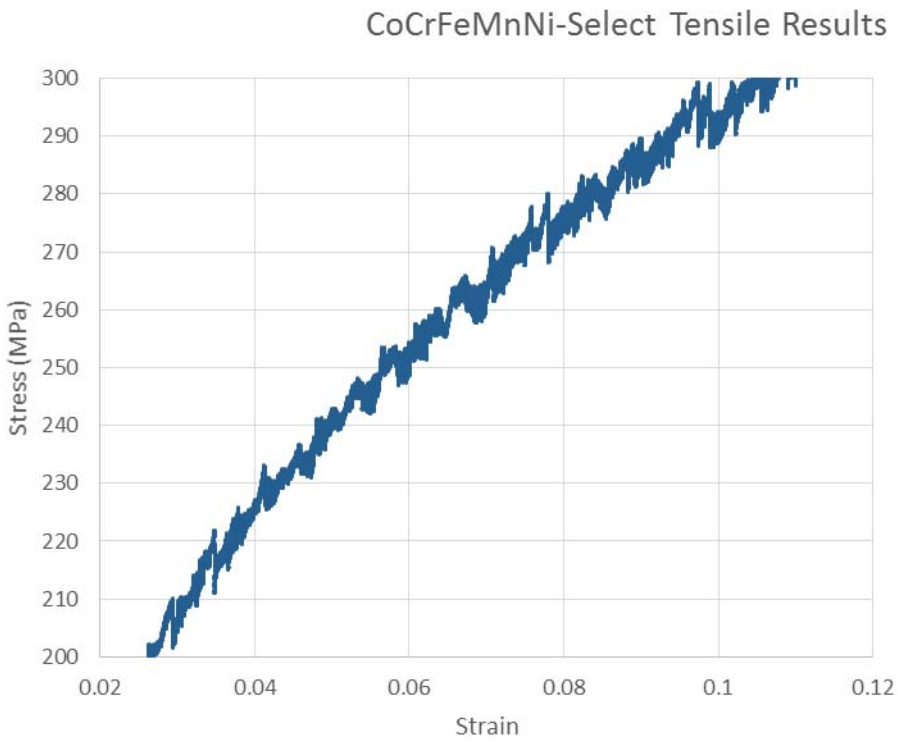
Sample contained residual wrought structure



Sample contained NO residual wrought structure

CoCrFeMnNi Residual Work Effects 600C





Sample contained residual wrought structure

Sample contained NO residual wrought structure

Summary

- Serrated flow in high entropy systems can be complex with many interacting variables
- The diffusivities of Mn and Cr in the alloys seem to support a diffusion driven dislocation interaction mechanism
- Additional quantification and analysis is necessary to understand the key variables and adjust them to control this effect

Acknowledgements

- Paul Danielson (metallography)
- Christopher Powell (mechanical testing)
- Ed Argetsinger (alloy processing)
- Joe Mendenhall (alloy processing)

Disclaimer

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