Enhanced Entropy Superalloy Development For Fossil Energy Applications (IPT Task 3.3)

Joseph J. Licavoli, Paul D. Jablonski, Michael C. Gao, Gordon Holcomb & Jeffrey A. Hawk

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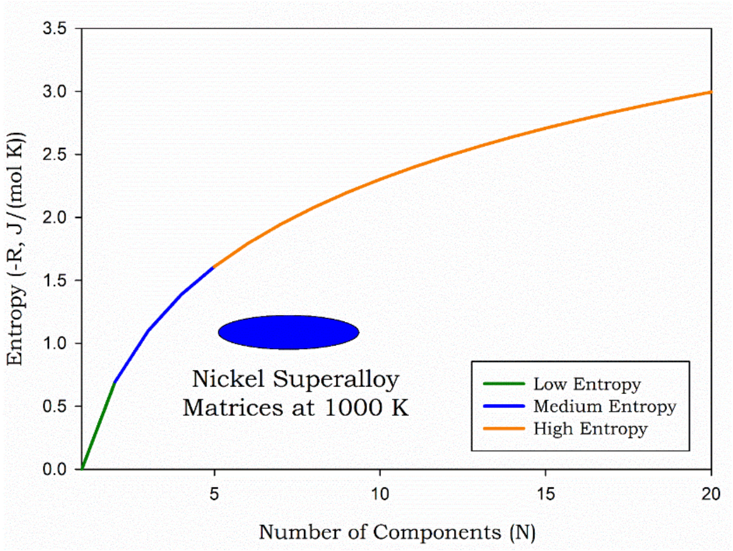
IPT Task 3.3-Advanced Alloy Concepts (Overview)

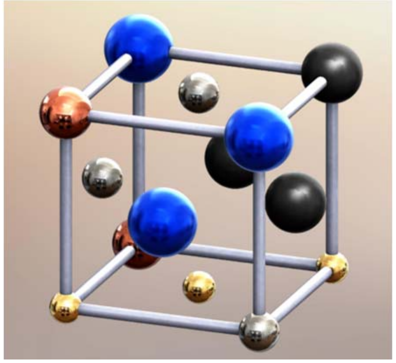
- **High Entropy Alloys**
  - Near industrial scale HEA production
  - ICME based entropy optimization
    - Application of CALPHAD
    - Off equiatomic compositions
  - Light weight HEA design
  - **Enhanced entropy superalloys**
    - **Designs based on commercial wrought alloy systems**
    - **Utilization of ICME for design/processing**
    - **Focused on high temperature mechanical properties**

High Entropy Concept

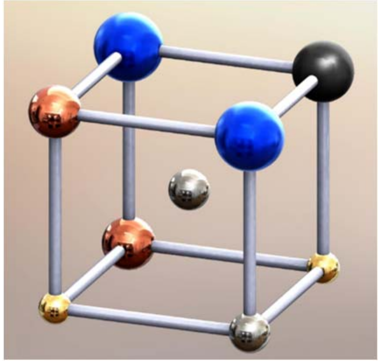
- **High entropy alloys (HEA's)**
  - – Multicomponent (N>4) systems
  - – Each component between 5-35%
  - – Configurational entropy term decreases Gibbs energy
    - Stabilizes single phase
    - Random lattice site occupancy
  - – Resultant phase has unique properties

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad \Delta S_{mix} = -R\sum_{i=1}^{N} x_i \ln x_i$$





FCC HEA



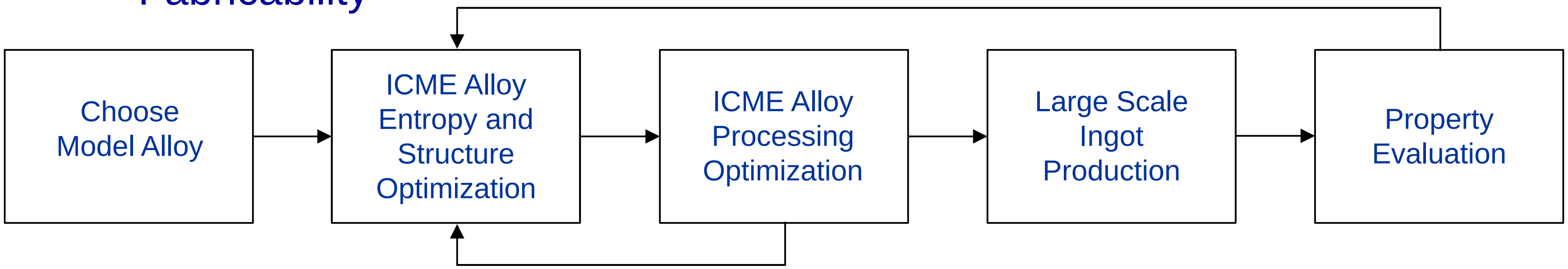
BCC HEA

Challenges in High Entropy Alloy Development

- **Shift in design paradigm leads to vast alloy design space**
  - Application of ICME
  - Limitations of CALPHAD techniques
    - Limited experimentally validated ranges (extrapolation issues)
    - Unavailable elements
- **We need a means by which to pick most promising candidate alloys**
  - Rapid throughput techniques (Miracle *et al.*)
  - Entropy enhancement of commercial alloy matrices
    - Utilize existing alloy chemistry
    - Modify existing chemistry to maximize entropy
    - Retain microstructural characteristics within reason

Alloy Design Process Overview

- **Choose alloy to mimic**
  - Haynes 282 chosen due to application in A-USC designs
  - Used CALPHAD to assess matrix composition
- **Utilize CALPHAD to systematically vary matrix chemistry**
  - Screen elements that lead to detrimental phase formation (TCP’s, etc.)
  - Increase elemental concentrations until an enhanced entropy state is achieved
  - Avoid “high cost” elements to minimize economic impact
  - Re-introduce gamma prime precipitates/other strengthening phases
- **Optimize for ease of processing**
  - Melting considerations
  - Homogenization
  - Fabricability



Processing and Chemistries

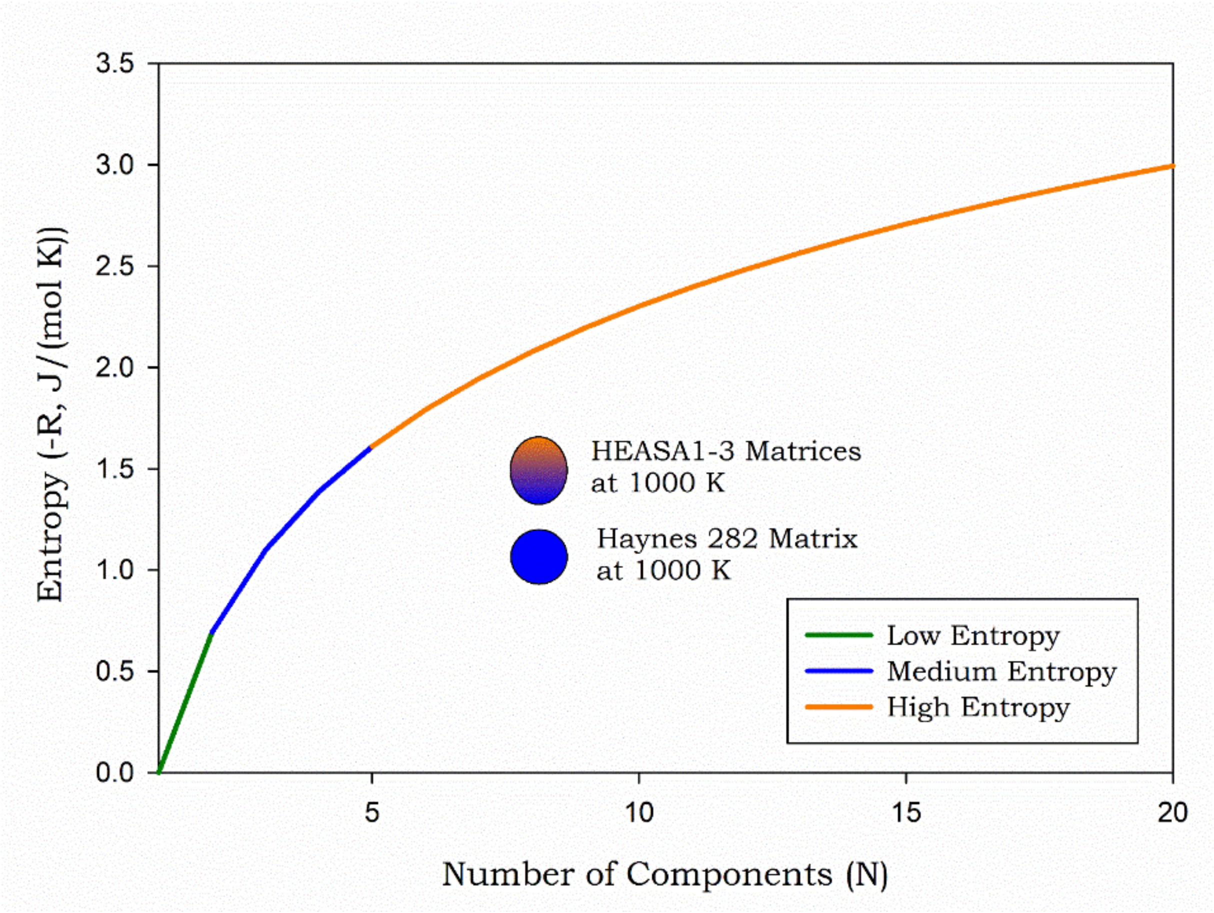
Three alloys were produced using the current design methodology.

- 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 800ºC
- SEM/TEM carried out on select mechanical test samples
- Environmental corrosion studies carried out

Actual Compositions of enhanced entropy alloys (wt%)

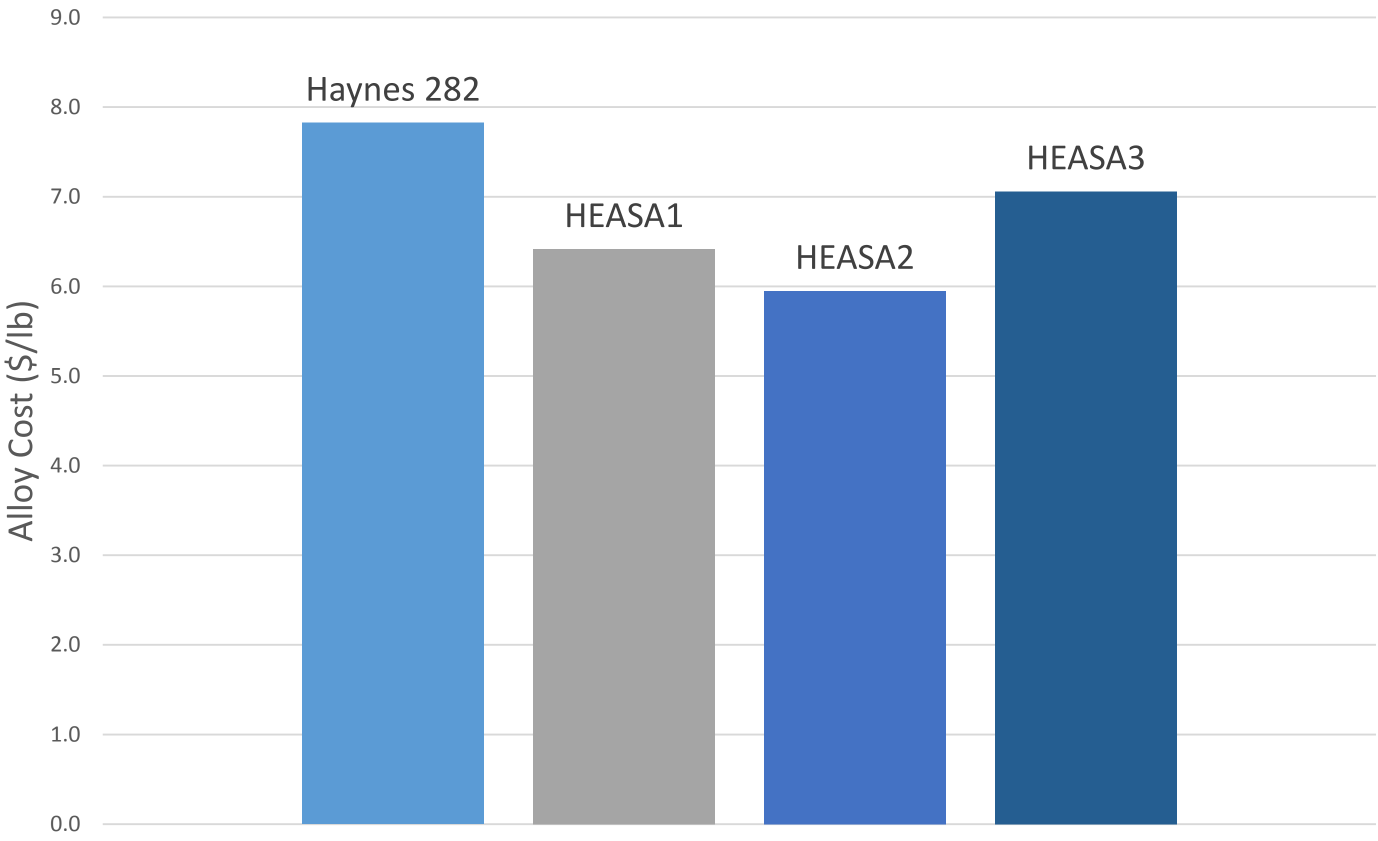
ID Name	Ni	Fe	Cr	Co	Mn	Al	Ti	Si	C	Ta
HEASA1	32.82	8.87	20	25.41	7.85	2.03	3.00	0.03	-	-
HEASA2	36.57	14.13	20.24	15.06	7.98	1.87	3.27	0.02	0.25	0.36
HEASA3	41.49	-	18.64	24.94	9.83	1.95	2.81	0.02	-	-

Alloy Entropy Level Comparison



HEASA1, 2 both achieved “high entropy” levels while HEASA3 fell in a “medum” entropy regime. The overall increase in entropy versus Haynes 282 was approximately 20-50% across the different designs.

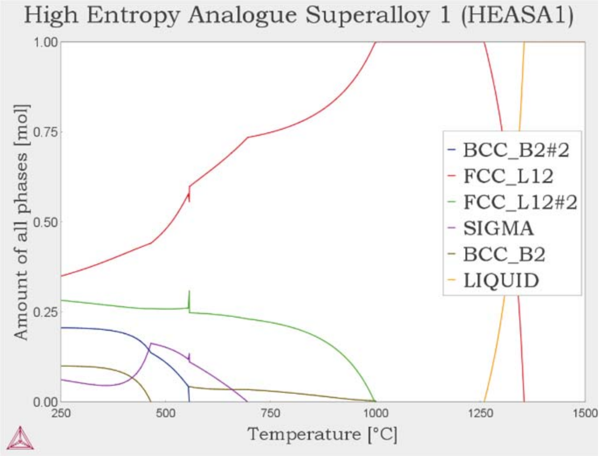
Alloy Raw Material Costs

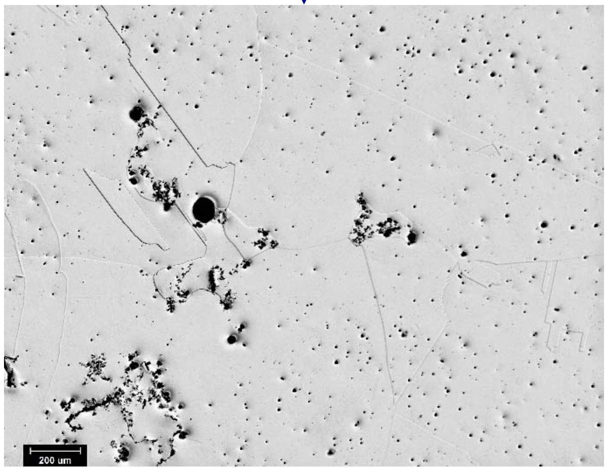


Each of the alloy designs reduced the raw material costs versus the "parent" material, largely due to reduction in Nickel, Molybdenum, and Cobalt. (*source: metalprices.com*)

Microstructural Results

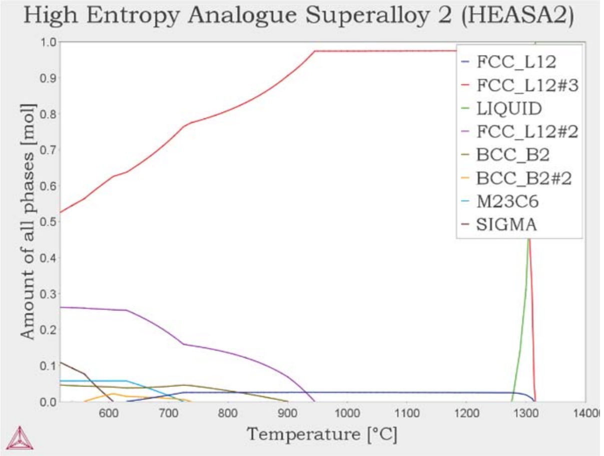
HEASA1

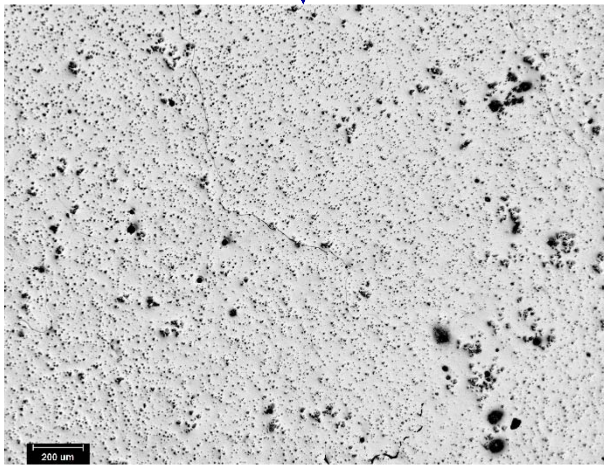




HEASA1-Homogenized

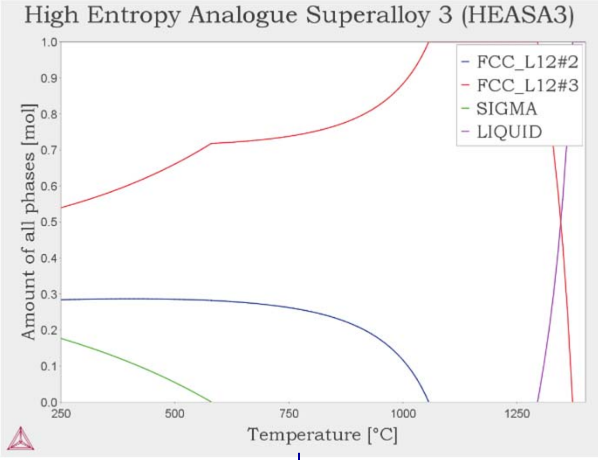
HEASA2

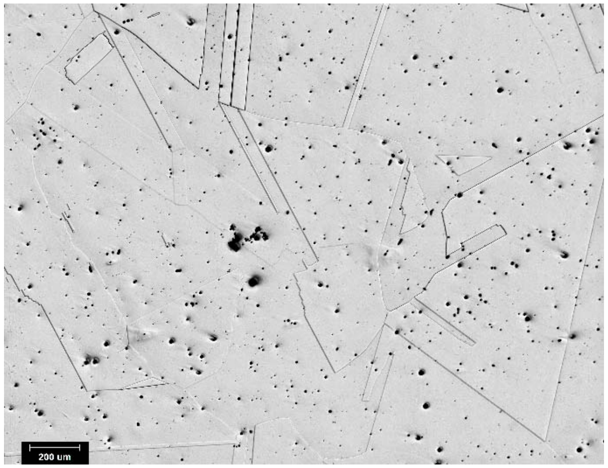




HEASA2-Homogenized

HEASA3

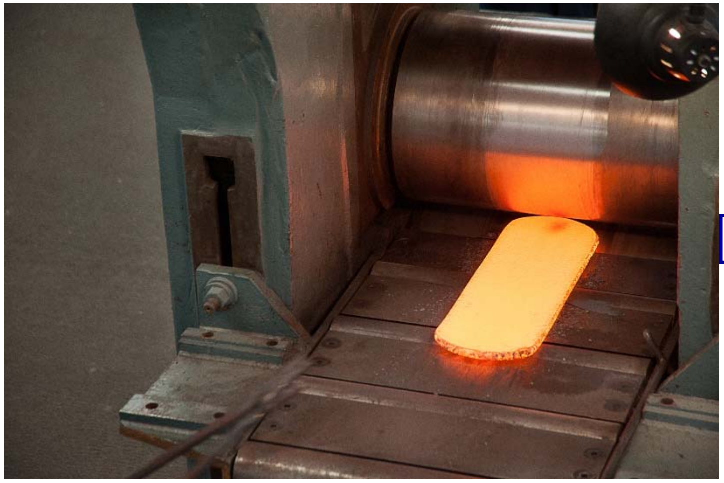


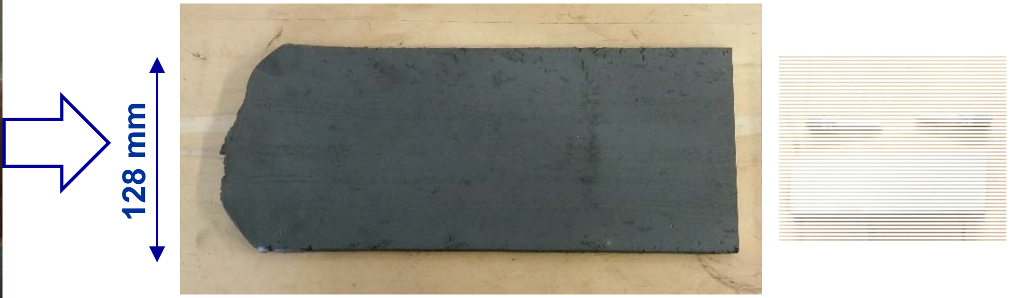


HEASA3-Homogenized

Forging Operations

Rolling Operations

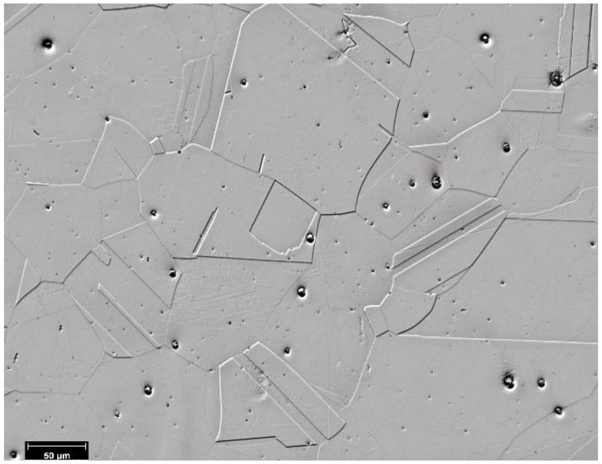




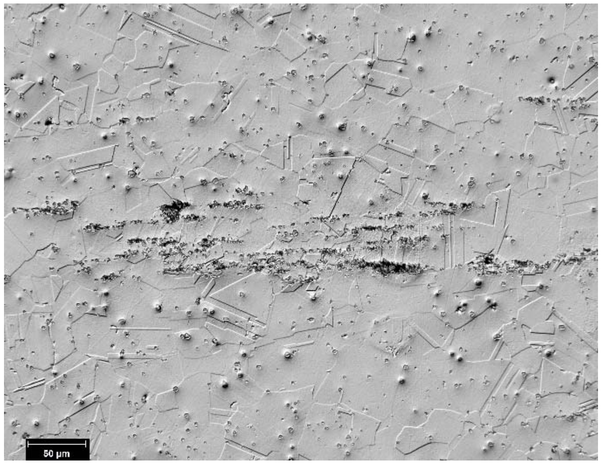
≈ 10 mm thick plate used for tensile specimens

Rolled Microstructures

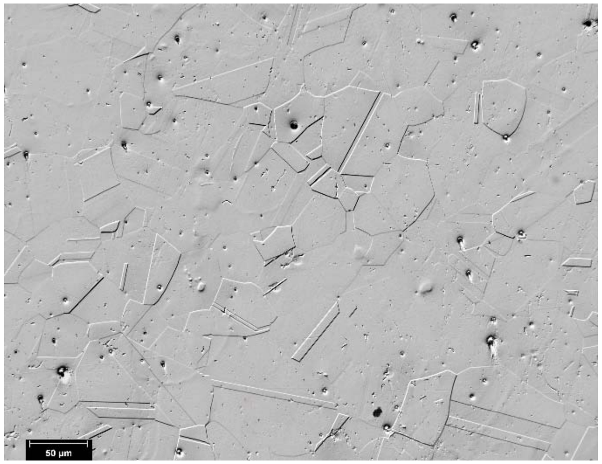
HEASA1



HEASA2

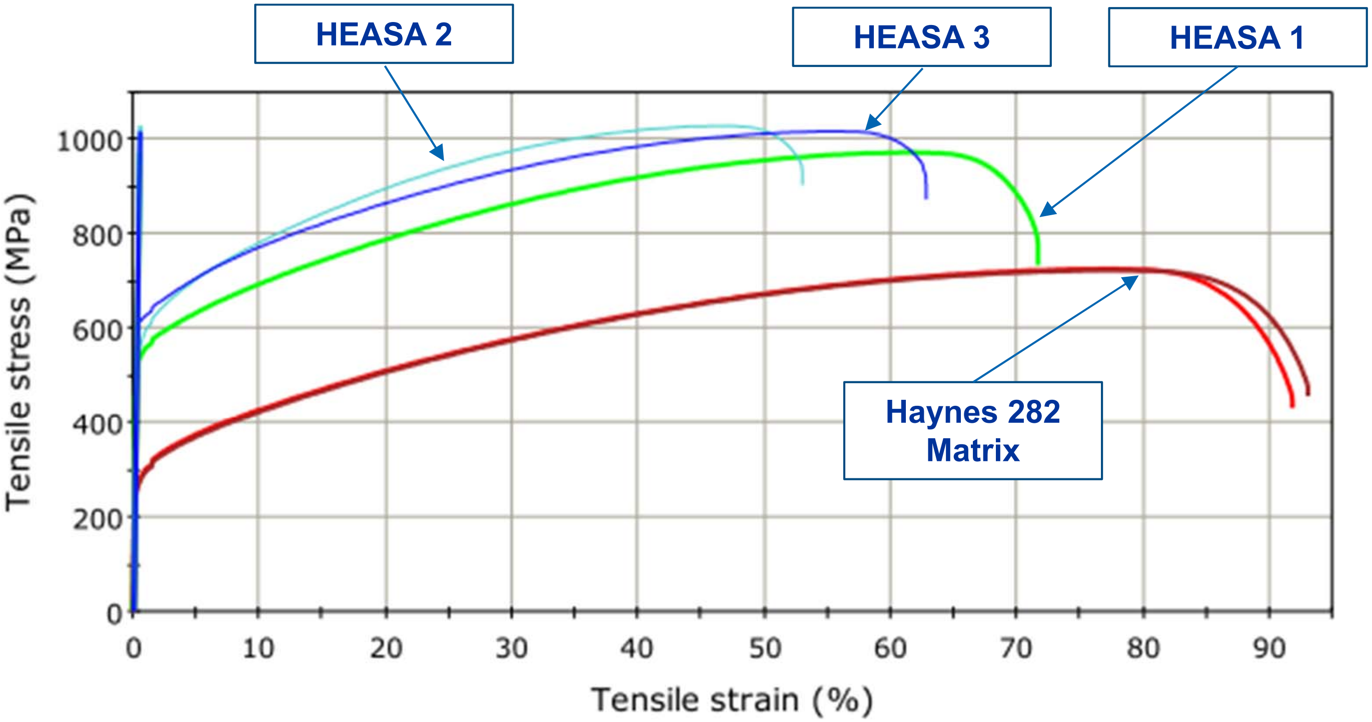


HEASA2



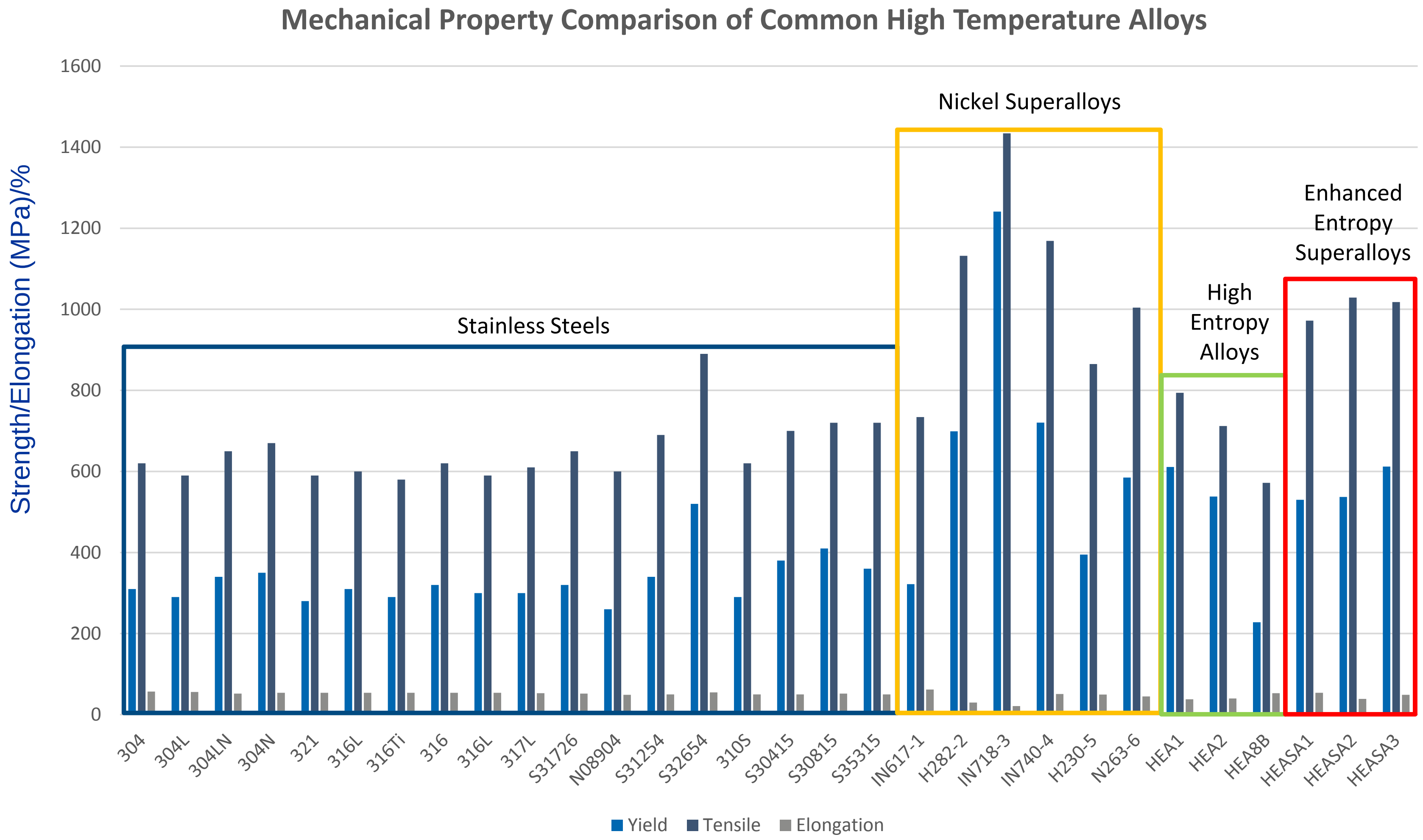
Rolled microstructures appeared as expected from CALPHAD predictions, with the exception of linear indications of titanium nitrides. Grain sizes were approximately 50-100 µm in HEASA1,3 and 25-50 µm in HEASA2.

Room Temperature Mechanical Behavior



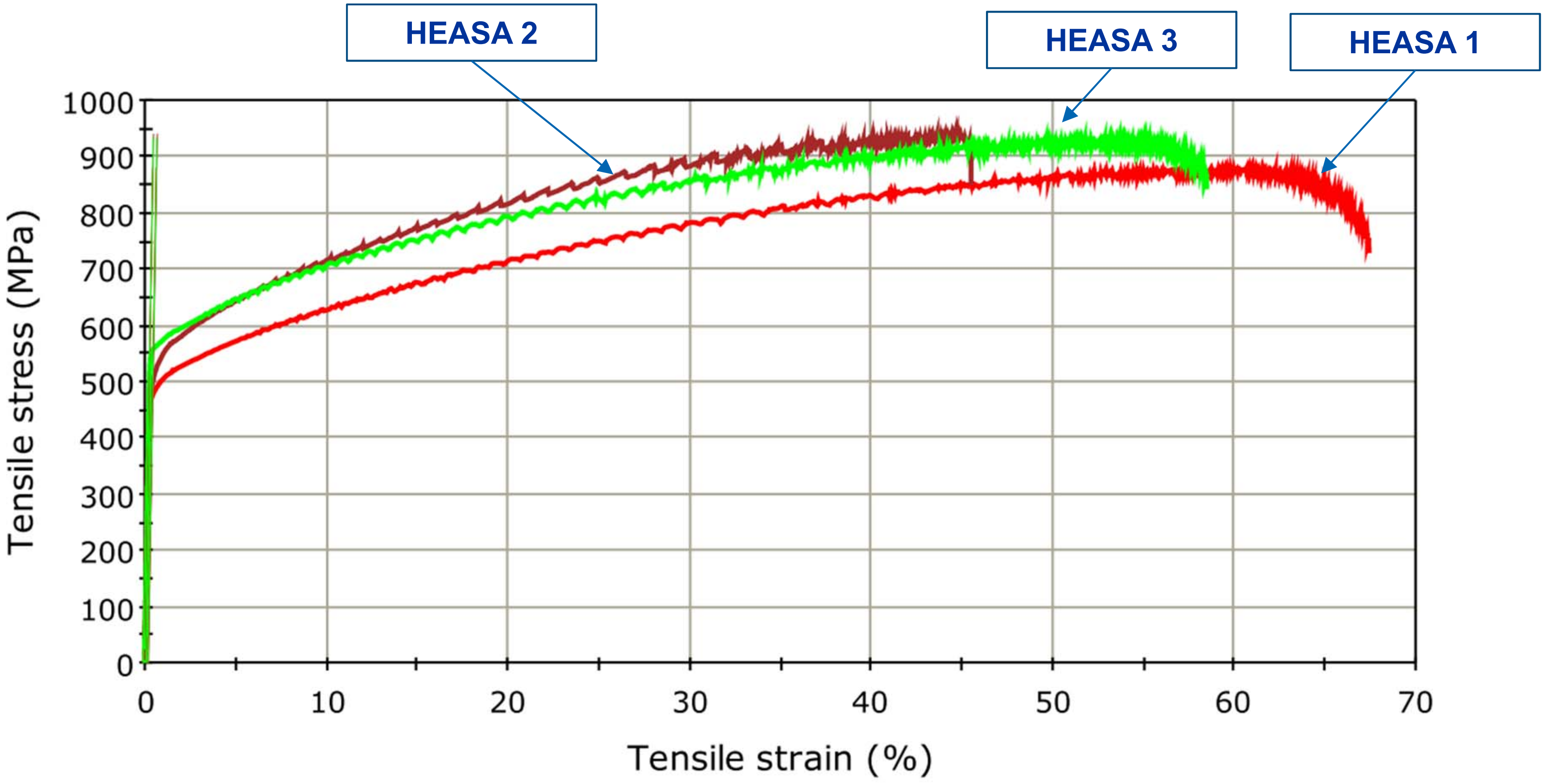
Room temperature behavior exhibited ductile failure with moderate work hardening. No significant anomalies were detected on fracture surfaces examined under SEM.

Room Temperature Mechanical Property Comparison



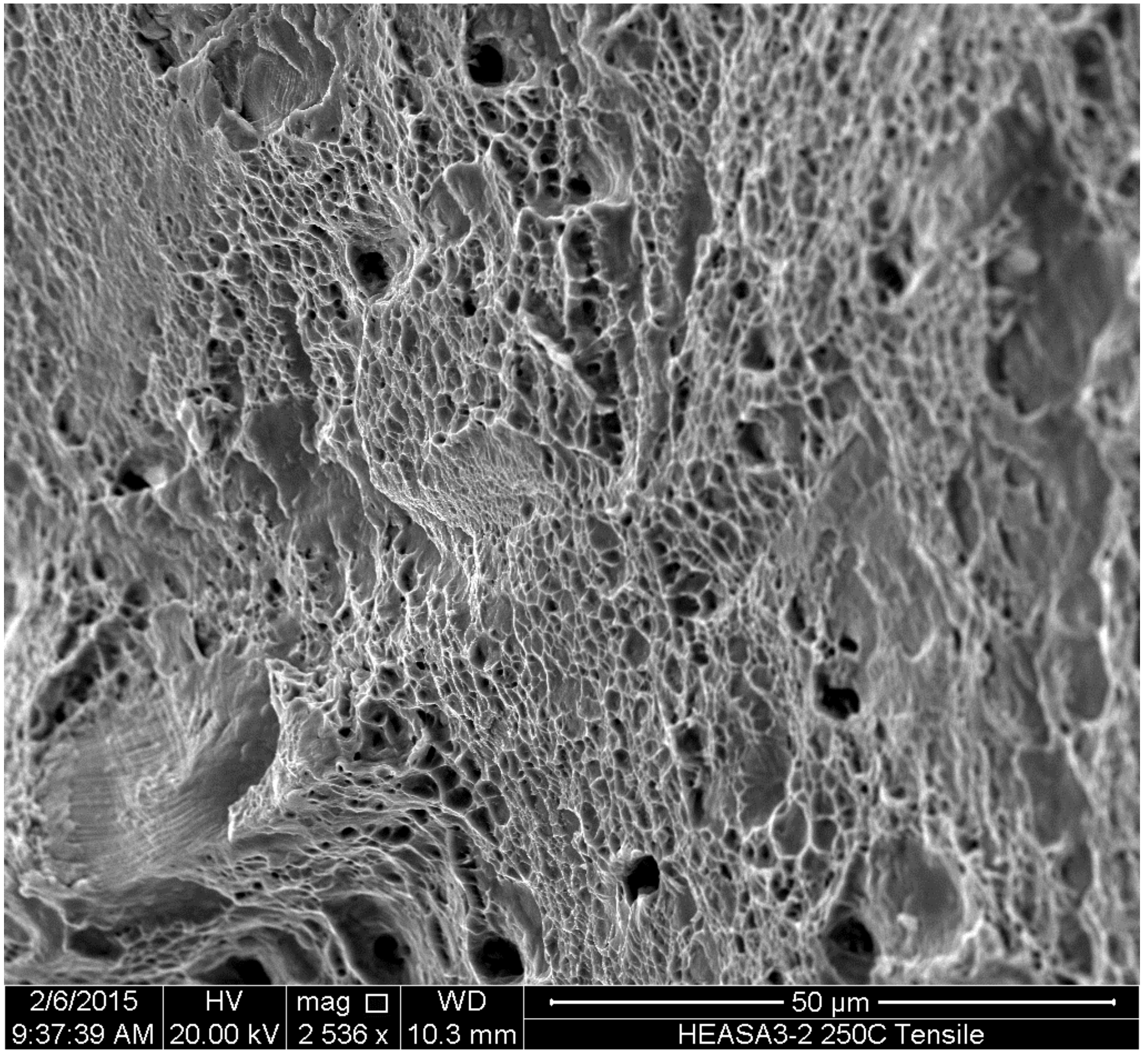
The room temperature behavior of the enhanced entropy superalloys is comparable to the selected nickel superalloys.

Elevated Temperature Performance (250°C)



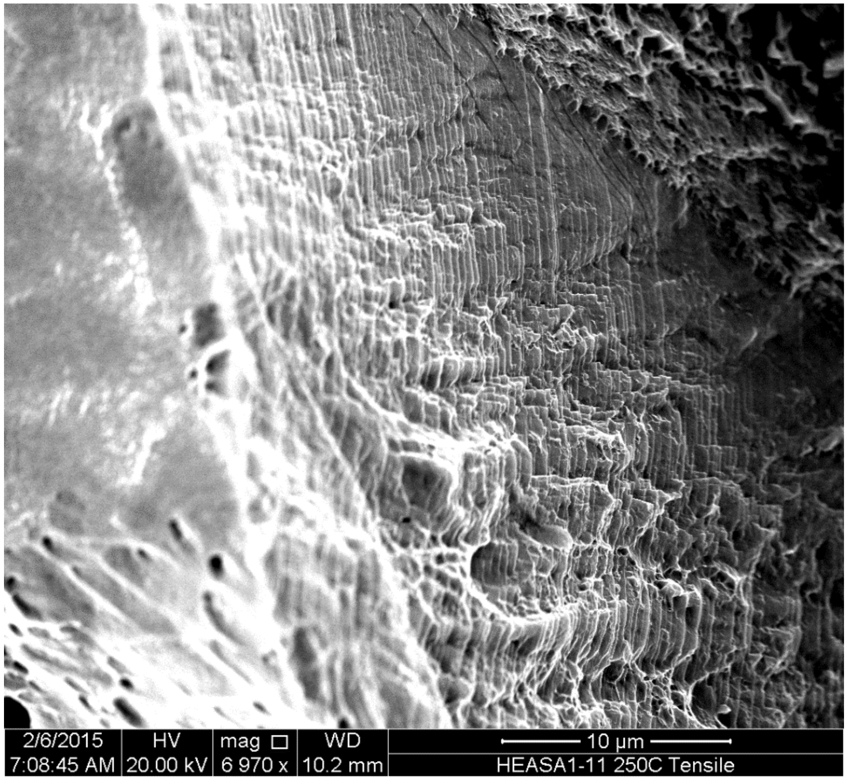
Above 250°C "jerky"/serrated flow was observed after yield accompanied by a repetitive knocking noise. This could be indicative of the Portevin Le Chatelier effect or twinning.

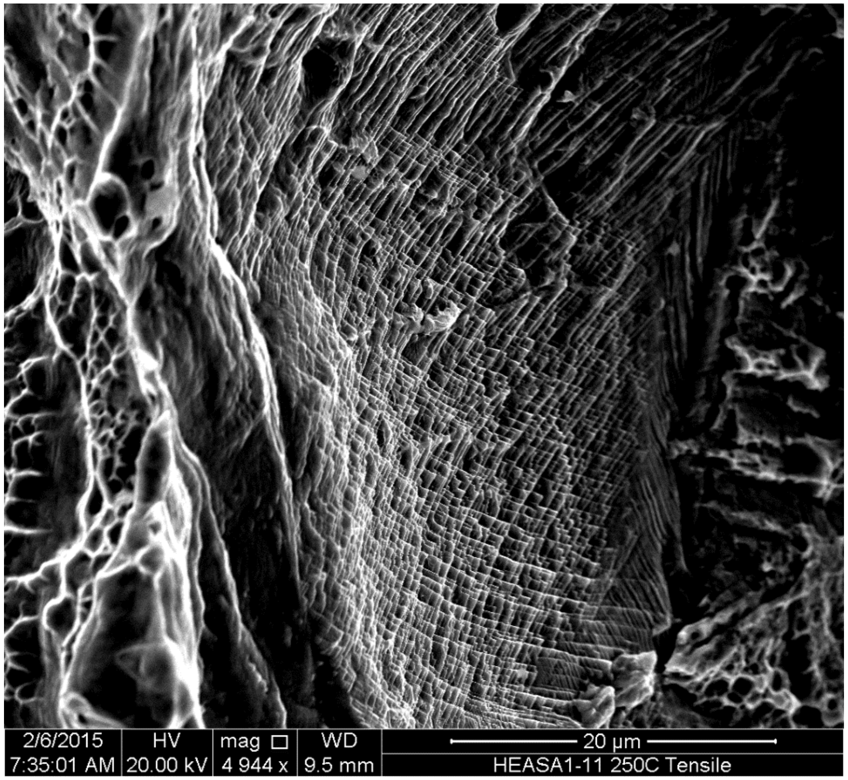
Representative Fracture Surface (SEM)



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

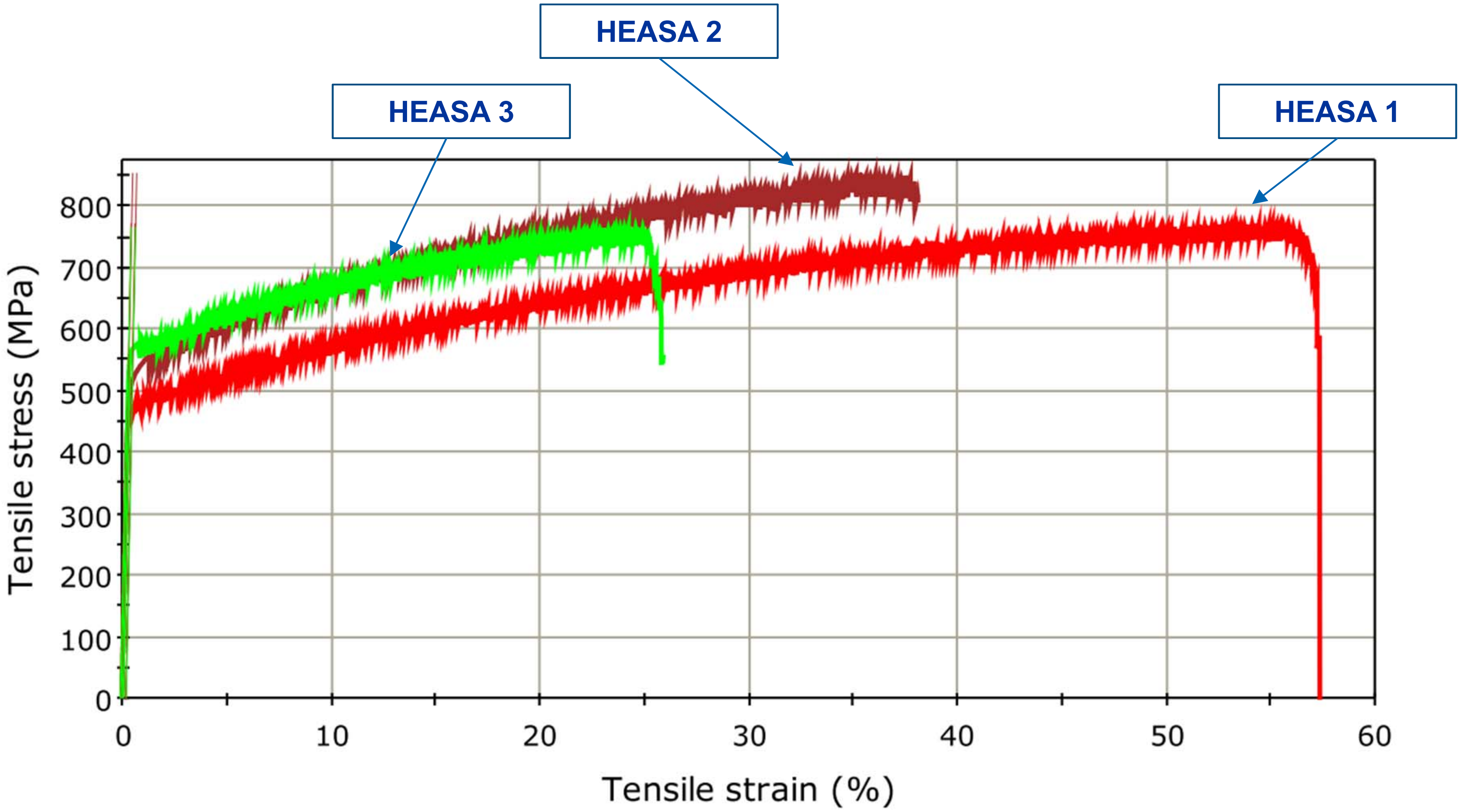
SEM of Striations on Fracture Surface





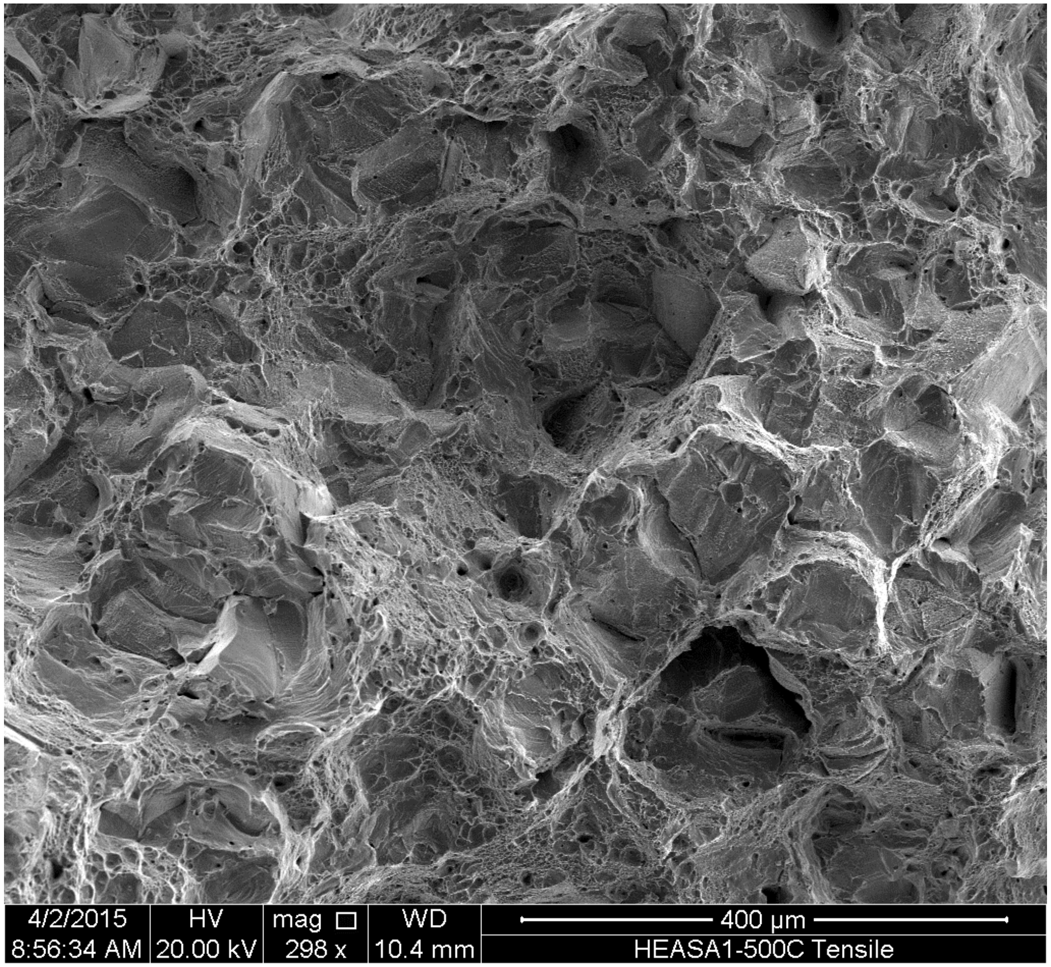
Ledged fracture surfaces appeared very frequently in all three alloys. The orientation of the ledged surfaces was approximately 45-55^{o} relative to the tensile axis. The orientation of the ledged surfaces matches similar features observed when the Portevin Le Chatelier effect becomes active.

Elevated Temperature Tensile Tests 500°C



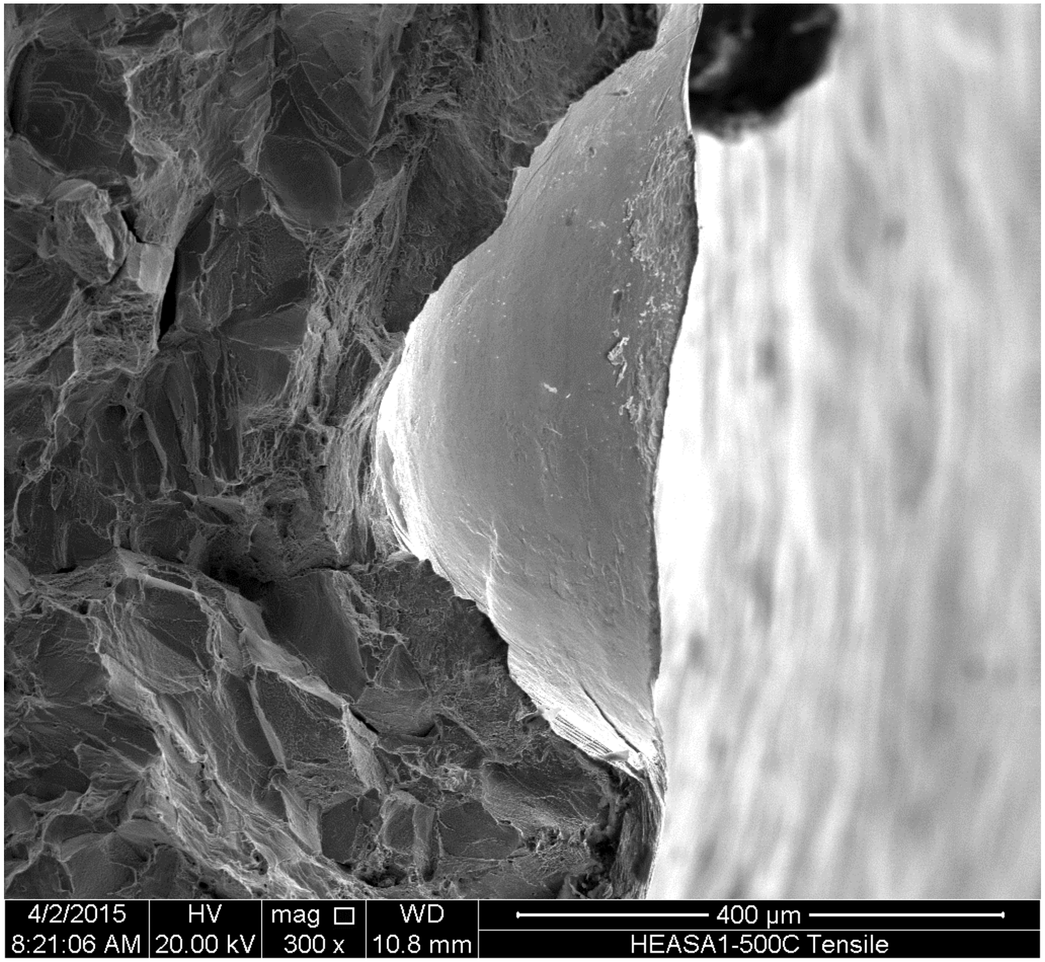
All three alloys again exhibited jerky flow at 500°C at a much higher frequency and with somewhat reduced ductility with the exception of HEASA1.

Representative Fracture Surface (SEM)



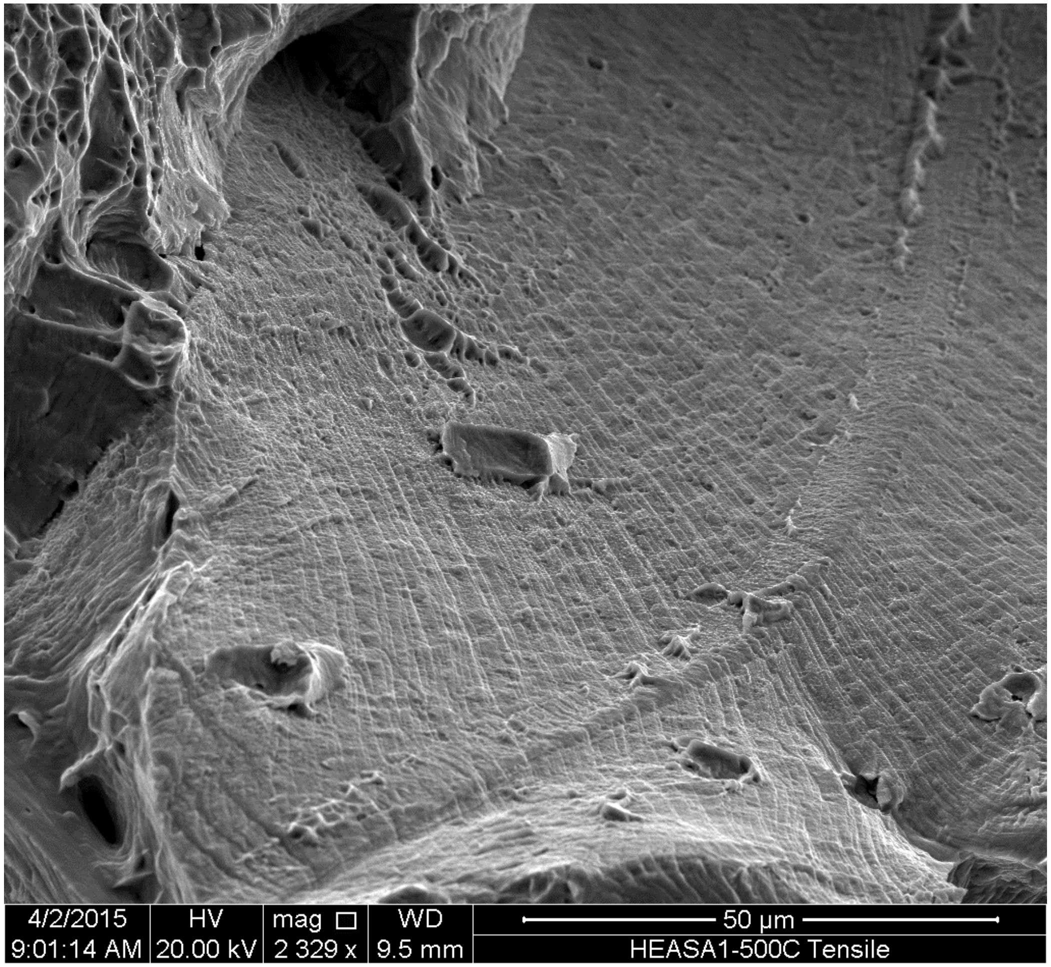
Fracture surfaces in all three alloys exhibited a mixed mode of failure including intergranular, transgranular, and ductile failure.

Fracture Initiation Point (SEM)



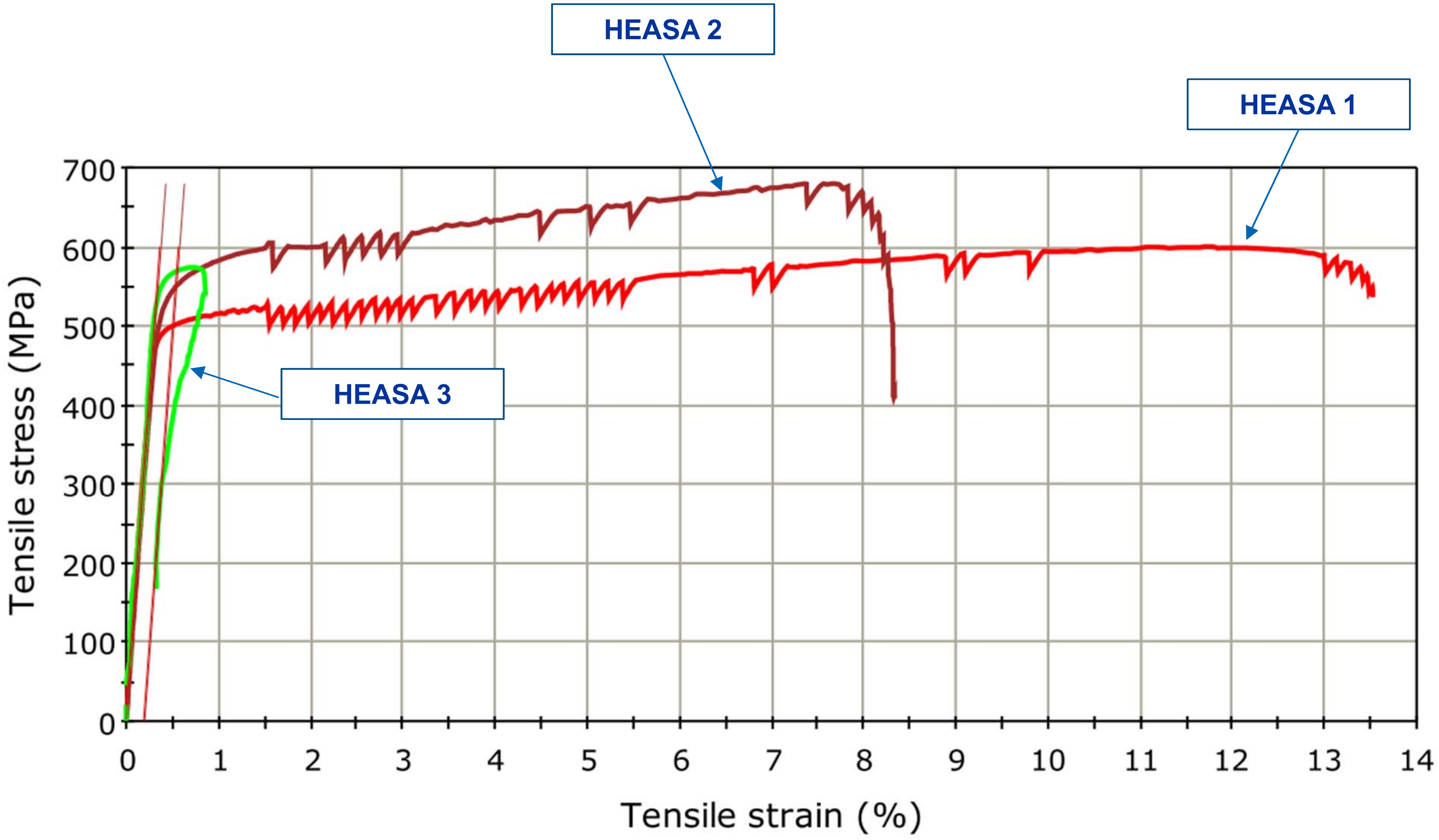
All three alloys exhibited increased notch sensitivity as is evident from fracture initiation at the attachment points for the high temperature extensometer shown above.

Striation on Fracture Surface (SEM)



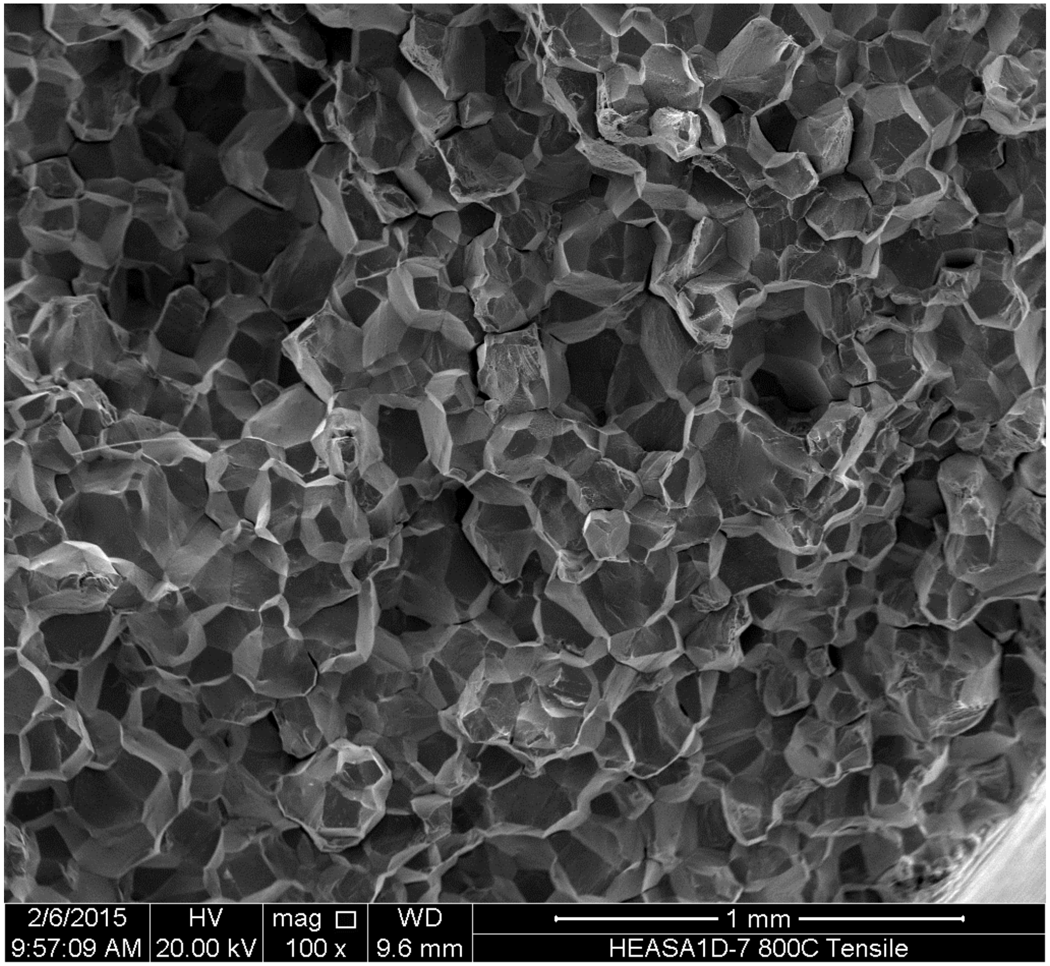
Striations on the fracture surface were again present on all three fracture surfaces.

Elevated Temperature Tensile Tests (600°C)

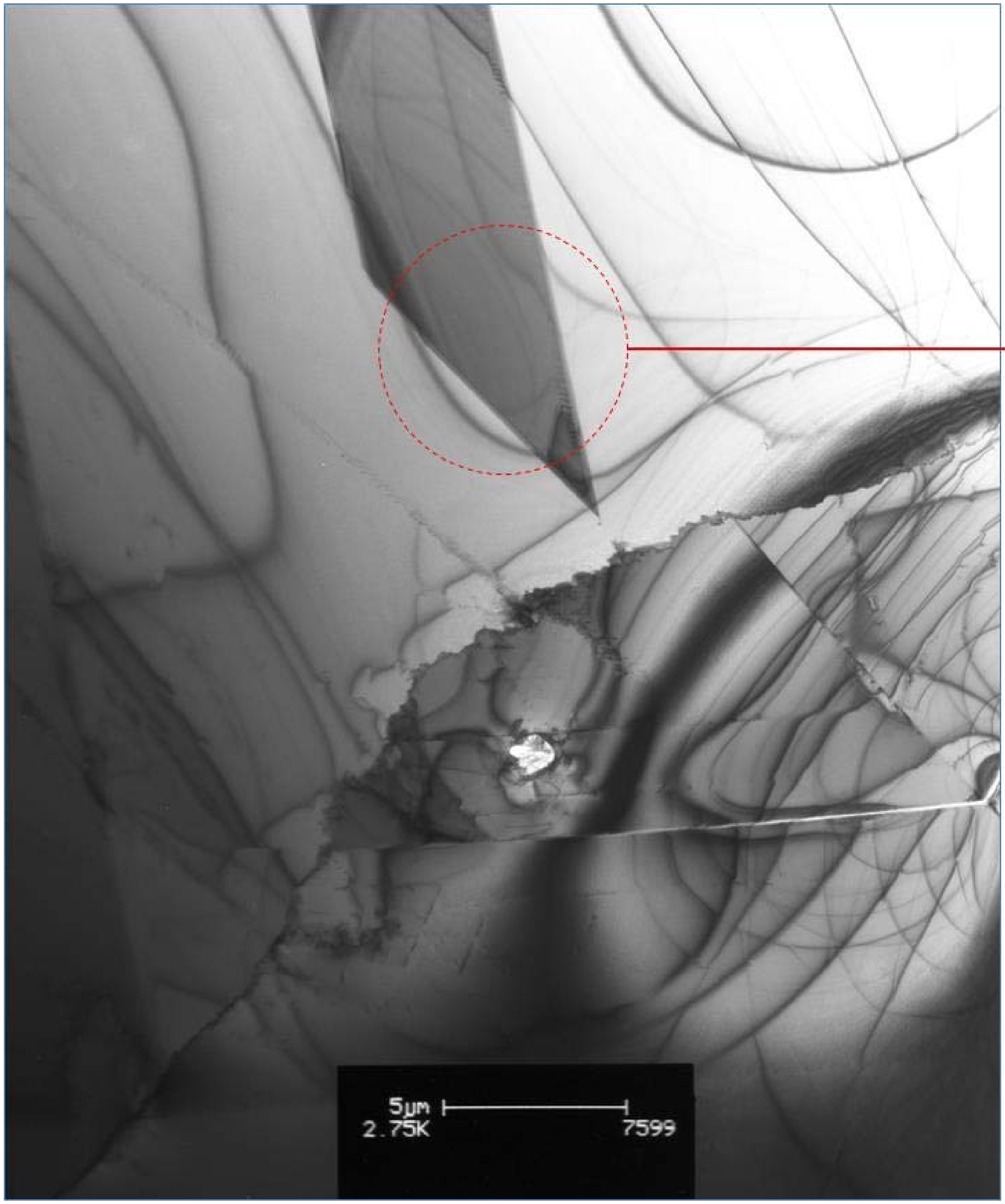


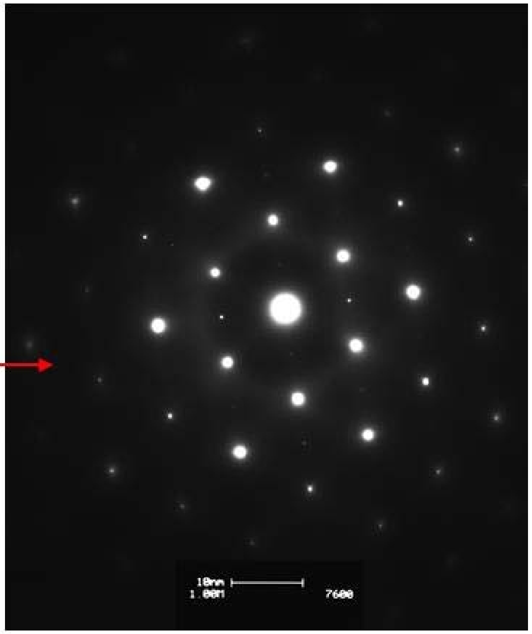
The jerky flow seemed to decrease in frequency considerably at 600°C. There also was a considerable decrease in ductility for all three alloys. This trend continued with brittle failure occurring before yield at both 700°C and 800°C in all three alloys.

Intergranular Failure at 800°C

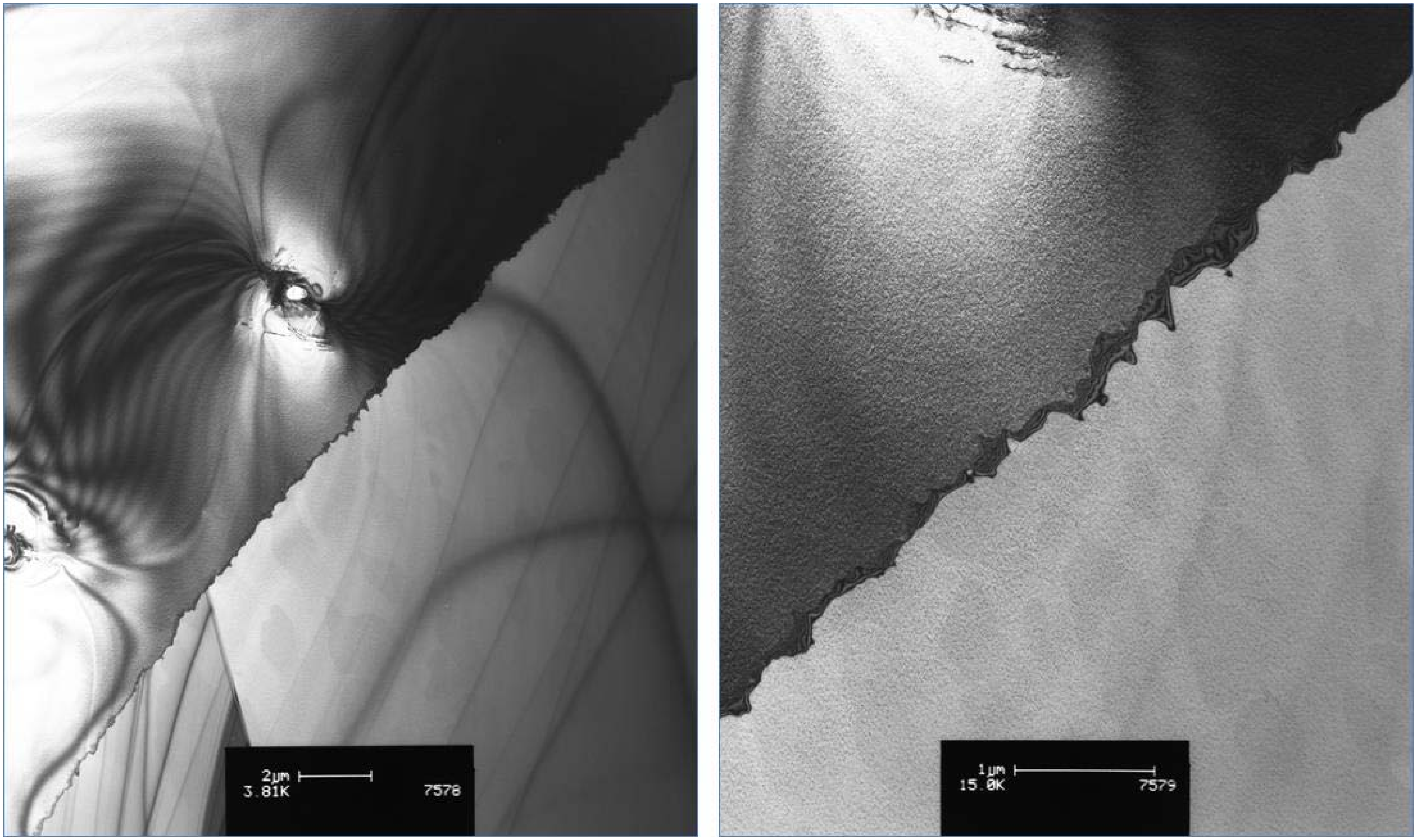


Severe intergranular failure above 600°C occurred in all three alloys. The nature of the failure appears to indicate that a detrimental factor is present at the grain boundaries in all cases.

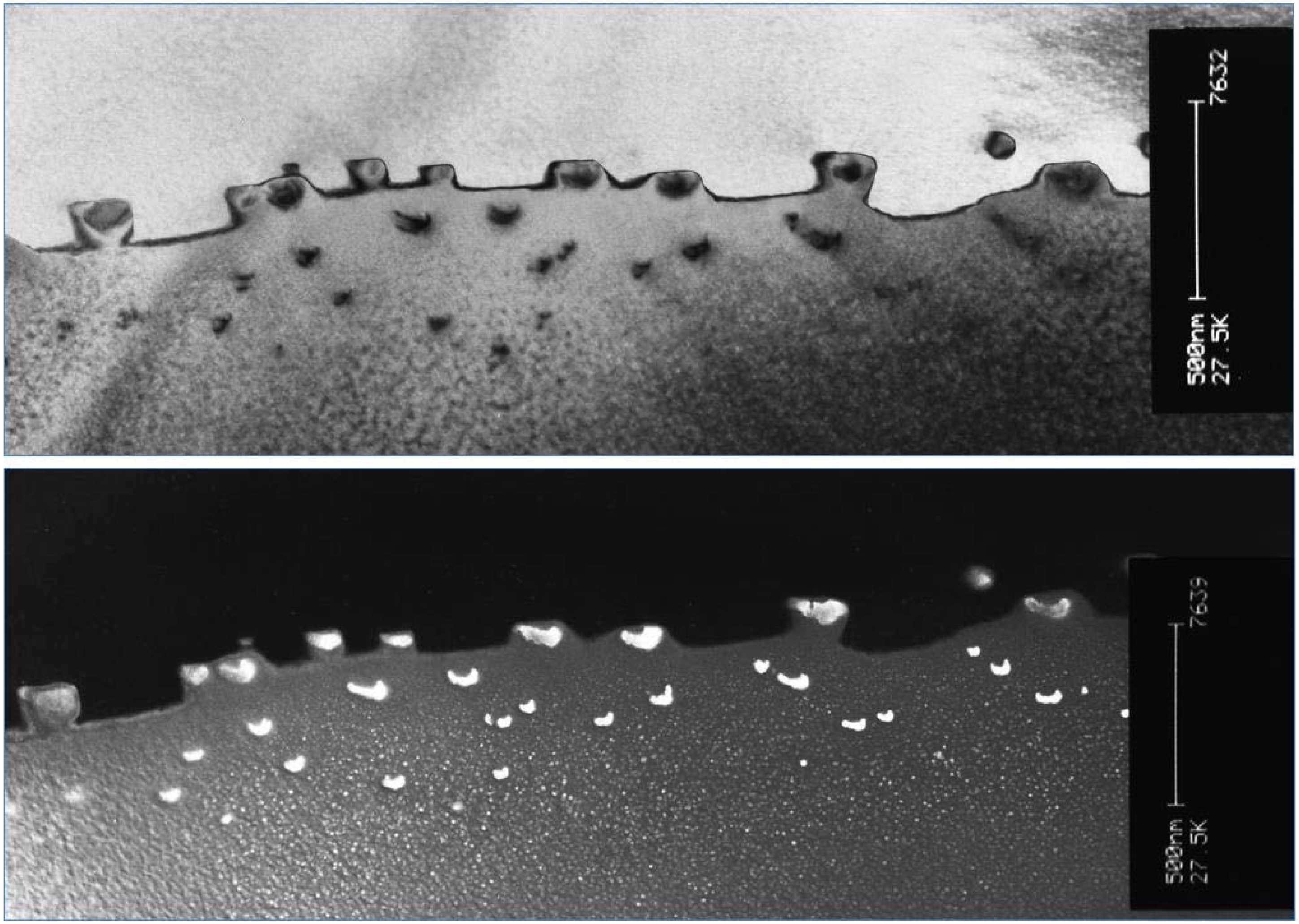




Example of twinning, TiN inclusion, and a convoluted high angle boundary. Here, the twinning provides a <110> zone axis pattern, overlaid with a <114> pattern. This represents the usual twinning relationship for *FCC* materials, but viewed at 90° away from the orientation that provides two <110> patterns.

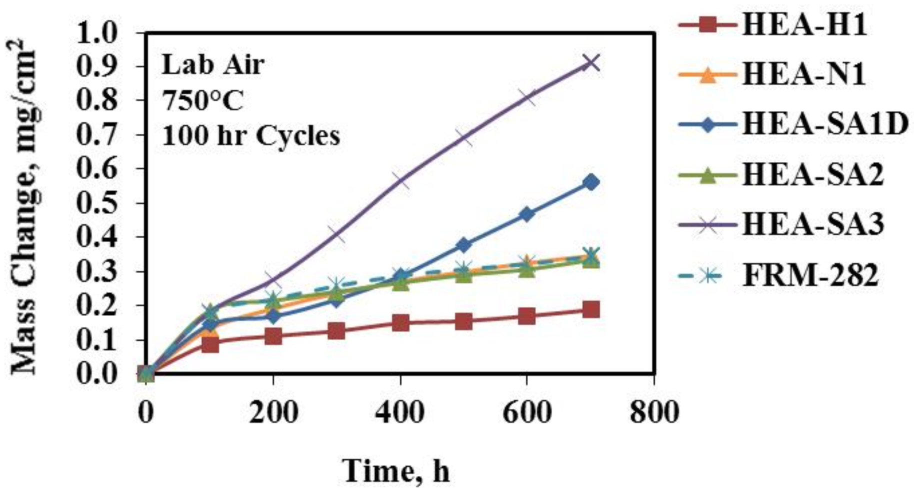


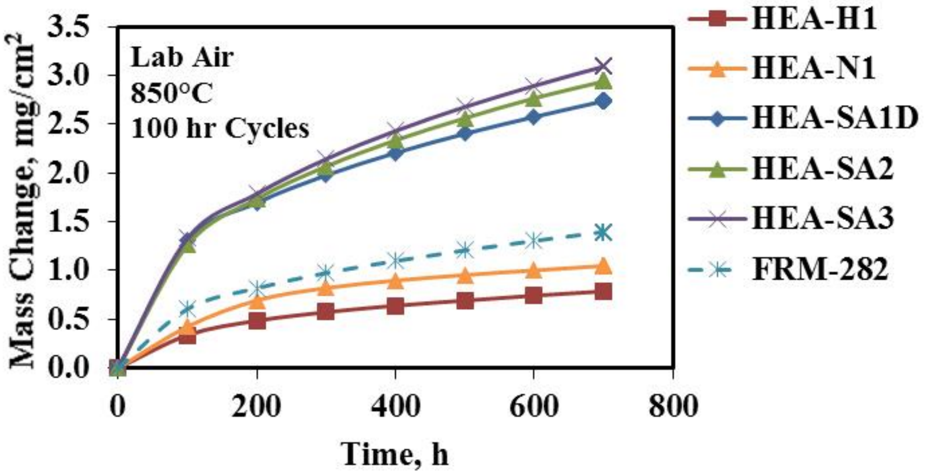
Another example of a wavy, ribbon-like high angle grain boundary. This one was explored under several different specimen tilt conditions.



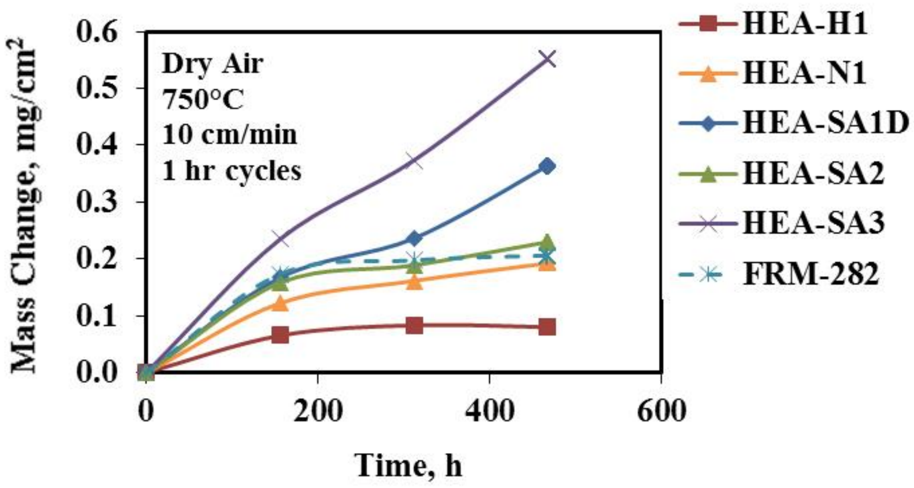
It was found that the grain boundary particles light up in DF when a γ' reflection is used to form the image. The tilt of the sample produced a somewhat random DP with suitably intense superlattice reflection easily located for this imaging. The relative sizes of typical γ' and *GB* particles is easily seen.

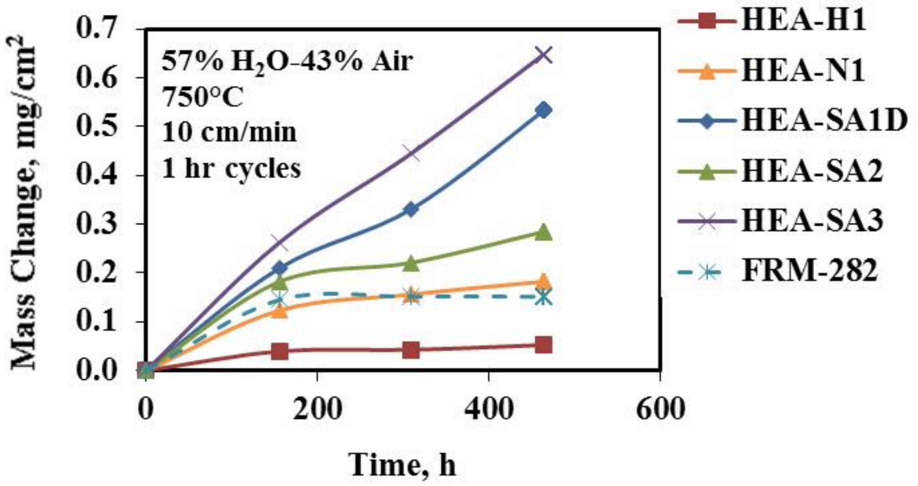
HEA-SA Air Oxidation (ongoing)





- All are performing at relatively low rates
- HEA-H1 and -N1 behave similar to 282





Summary

- **ICME based alloy design resulted in several feasible/fabricable compositions**
  - – Room temperature properties were competitive with parent alloy
  - – High temperature mechanical response was dominated by serrated flow and grain boundary embrittlement
  - – TEM investigations revealed potential grain boundary issues
- **Overall the design philosophy seems to be efficient and may be applied to other systems aside from nickel alloys**

Ongoing Work

- **Determination of grain boundary embrittlement mechanisms and remediation**
- **Application of alloy design philosophy to other alloy systems to hybridize them with the high entropy concept**
- **Design philosophy improvement**
  - Use of ICME toolset to design for "gradient" type behavior
  - Develop more holistic view of microstructure design aside from entropy enhancement
- **Ongoing corrosion studies**
- **Creep evaluation on modified alloys**

Project Acknowledgements

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Disclaimer

Questions?