Advanced Alloy Development

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NATIONAL ENERGY TECHNOLOGY LABORATORY

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Structural Materials Team

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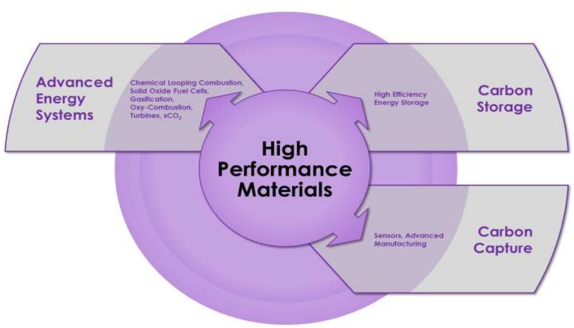
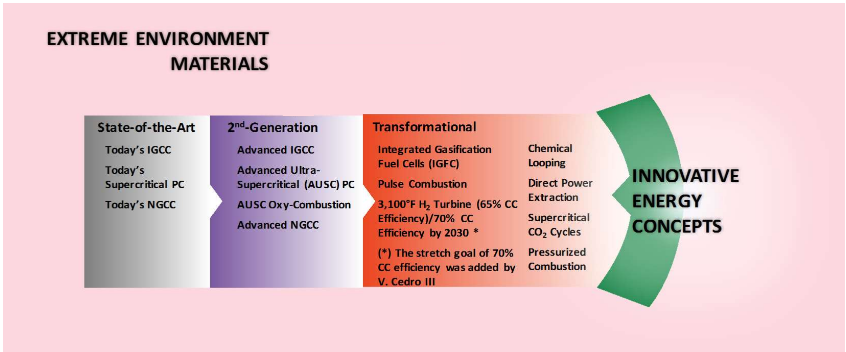
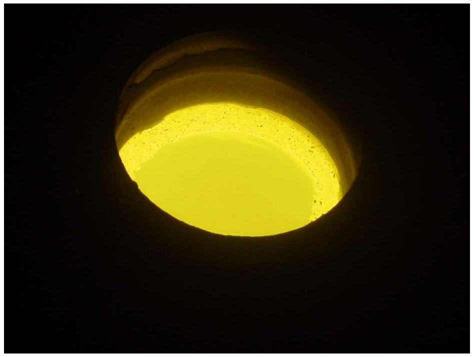
Overall Objective

All the details—a balancing act

- Reduced cost, extended life, increased efficiency, reduced pollution.
- Balancing act—trade offs.
- Focusing on operating conditions or desired performance; sometimes considering existing options.
- Critical element levels/ranges.
- Computational thermodynamics but also other considerations such as historical costs of raw materials



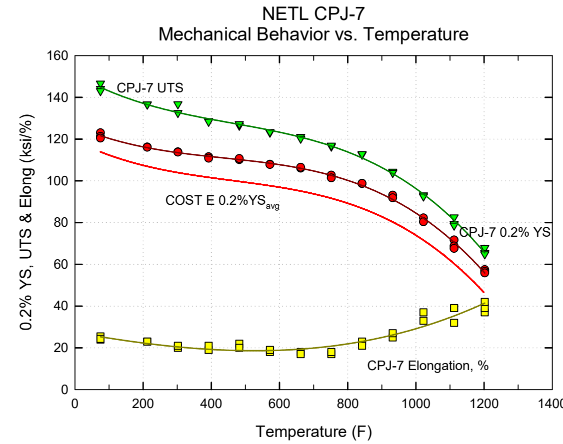


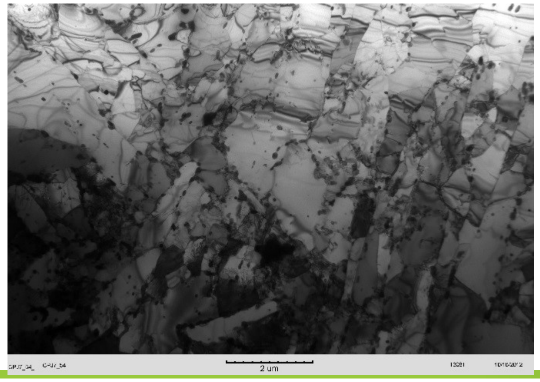


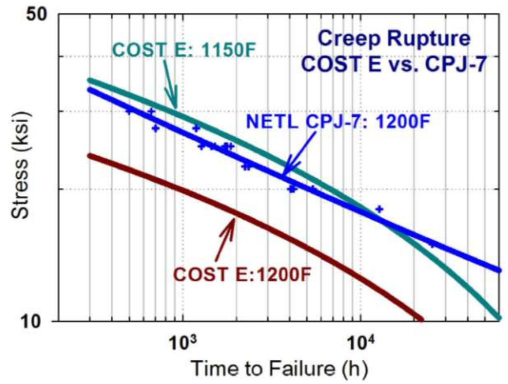
High Performance Steel

CPJ 7

- Excellent strength and ductility at temperature compared to commercial alloys within its class.
- 50F performance advantage in creep compared to commercial alloys within its class. Testing has surpassed 20,000h.
- Excellent corrosion and oxidation resistance due to the relatively high Cr level.
- The alloy was developed through careful control and consideration of major, minor and tramp elements that might be found in this class of material.
- Conventional induction melting was used to produce the first 20 or so heats.
- An advanced homogenization heat treatment was employed to ensure the level distribution of alloy elements and thus long term stability.
- U.S. 9,181,597 B1 (11/10/2015) and
  U.S. 9,556,503 B1 (1/31/2017)



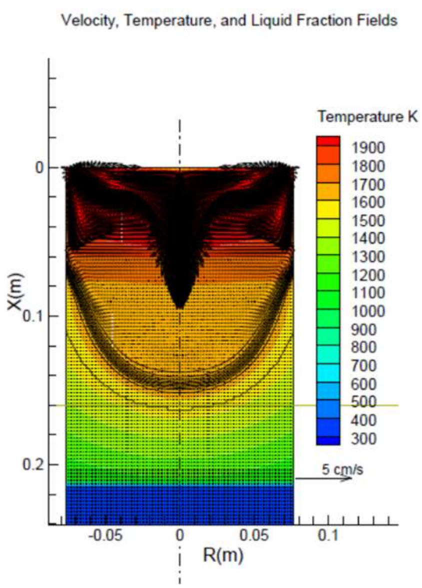




High Performance Steel

CPJ 7—larger scale material: ESR melts

- ESR has been utilized to make several 75+ kg heats.
- Computational fluid dynamics have been utilized to help refine the process.
- Excellent ingot quality has been achieved.
- Four heats have been fabricated into plate and provided to PNNL for weldability trials.



High Performance Steel

CPJ 7—larger scale material: ESR melts

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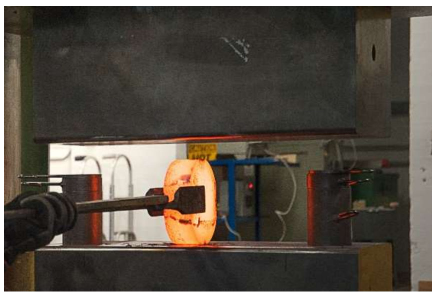
- For handling purposes, each heat is sectioned into 2in nominal slices.
- These round sections are first forged square then subsequently step forged followed by squaring operations and finally hot rolling.
- Hot rolled plates are subsequently autenitized, air quenched and tempered.



Five of a total of 36 plates of CPJ 7 sent to PNNL for friction stir welding studies.

Additional Steels

Evaluating other alloys

- Our work on the MARBN alloy looked promising (better performance than that reported by Abe). We are currently evaluating a cast version (with minor alloy modifications) as well as a couple of higher Cr versions for better corrosion resistance.
- Alloy P92 is a workhorse in high creep condition FE applications. However, it has gained a reputation of being hard to work with and sometimes fails prematurely.
- Our review of the alloy chemistry specification has revealed the following:
    - Some chemistry combinations result in gas bubble formation during solidification.
    - Some chemistry combinations result in primary BN which is often reported at early creep failure initiation sites.
    - Without proper homogenization solute rich and poor regions will persist and become unstable over time leading to undesirable phases.
    - We have several heats under test to evaluate these factors.

Cast Ni Alloys for AUSC

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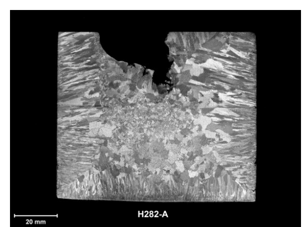
Turbine casings, valve chests, etc.

- Wrought property performance (creep) in cast Haynes 282.
- Castings on the order of 17,500lb have been poured.
- Critical to this was the development of a computationally optimized homogenization heat treatment.

- A second alloy with comparable properties is desired from a OEM point of view.
- IN740H appeared to be a strong candidate.
- Creep samples of cast IN740H have suffered from minimal creep ductility and thus reduced life.
- The source of the reduced life appears to be the nearly continuous grain boundary carbide film that forms on the large cast grains.
- Modifications to the alloy and heat treatment have been successful in raising the ductility, but not the to desired level.
- Another alternative alloy will be sought.

VAR Ingot: 24in Diameter x 71in long, ~10,000lb



Modified IN725

Improving high temperature strength and stability

- Derivative of IN625 with Ti added.
- Precipitate-strengthened Ni-based superalloy.
- High corrosion resistance.
- Applications where resistance to aqueous corrosion, pitting or stress corrosion cracking in sea water is essential.
- Relatively high strength at low to medium temperatures.
- **Properties at high temperatures? Phase stability?**

Table 1. Composition of IN725 from Ref. [1] in wt.%.

	Ni	Cr	Mo	Nb	Ti	Al	C	Mn	Fe
Max	59.0	22.5	9.5	4.0	1.7	0.35	0.03	0.35	Bal.
Min	55.0	19.0	7.0	2.75	1.0	-	-	-	

Modified IN725

Procedure

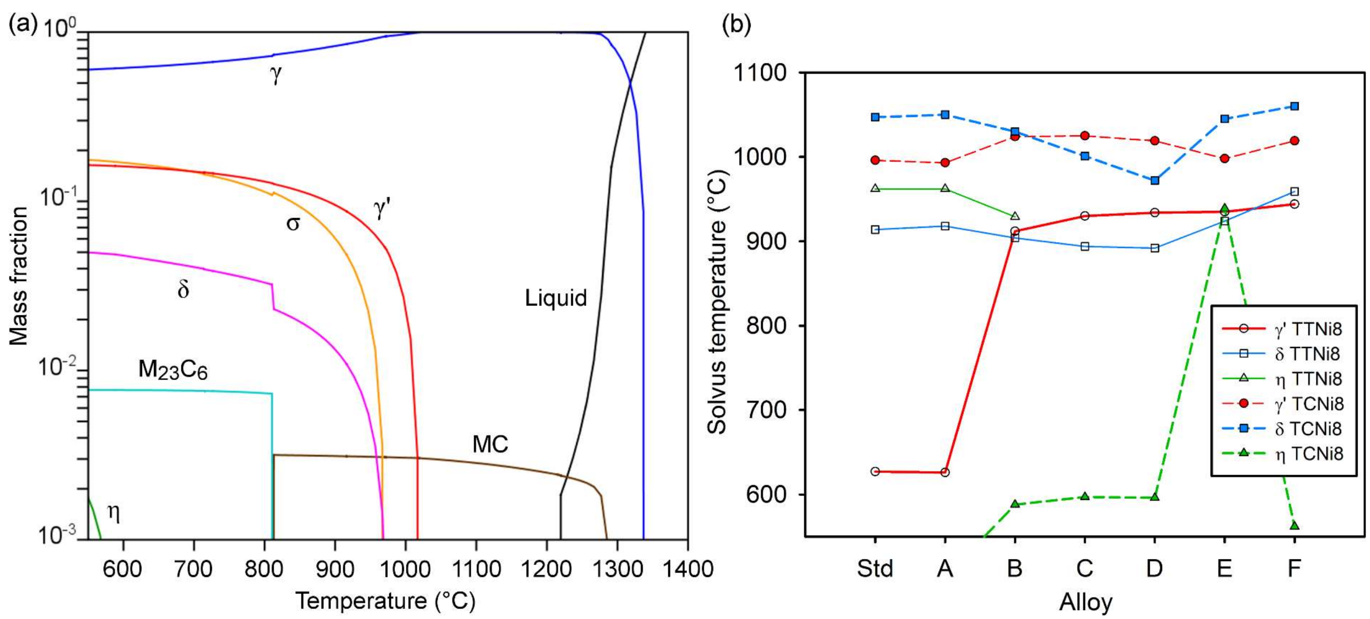
- Thermodynamic design using Thermo-Calc and JMatPro
- 7 heats considered (Table 2)
- 7 kg ingots were vacuum induction melted (VIM) using high-purity industry-grade melt stock.
- Homogenization was computationally optimized.
- Hot worked to form 12.5 mm thick plates.
- Standard aging treatment at 730°C / 8h, 56°C/h to 620°C, hold for 8h.
- ASTM E-8 and ASTM E-139 tensile and creep testing.

Table 2. Changes in composition of the IN725 variants investigated from XRF compositions in wt.%.

Alloy	Addition	Ti/Al
STD	-	4.26
A	Low Ta	5.43
B	Low Ta	1.33
C	Low Ta	1.07
D	Low Ta	0.73
E	10 times increase in Ta	0.72
F	32% increase in Nb	0.76

Thermodynamic

CALPHAD Predictions

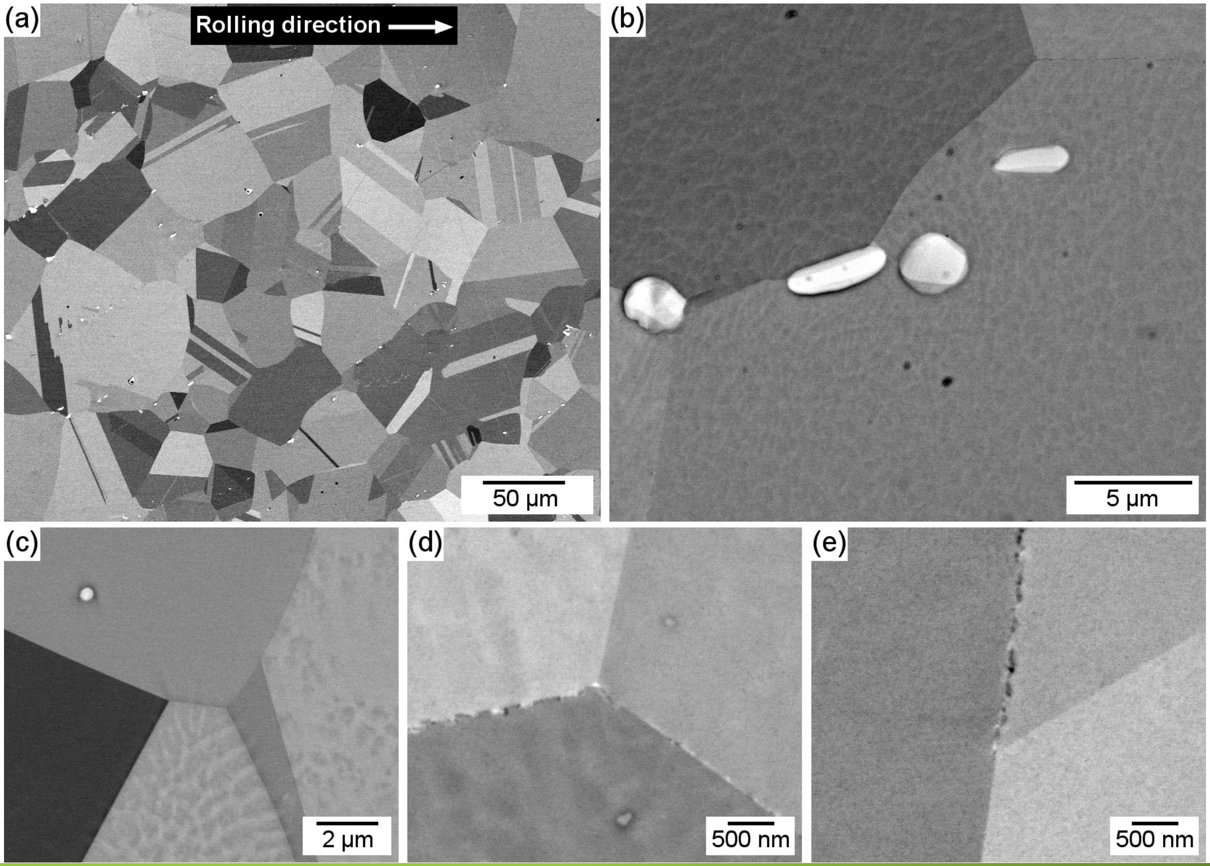


- Stability of $M_{23}C_6$, MC, γ′, δ, σ precipitate phases.
- Decreasing the Ti/Al ratio results in an increase/decrease in the fraction of γ′/ δ.
- Significant variations in solvus temperatures and η phase stability between TCNi8 and TTNi8.

IN725 Microstructure

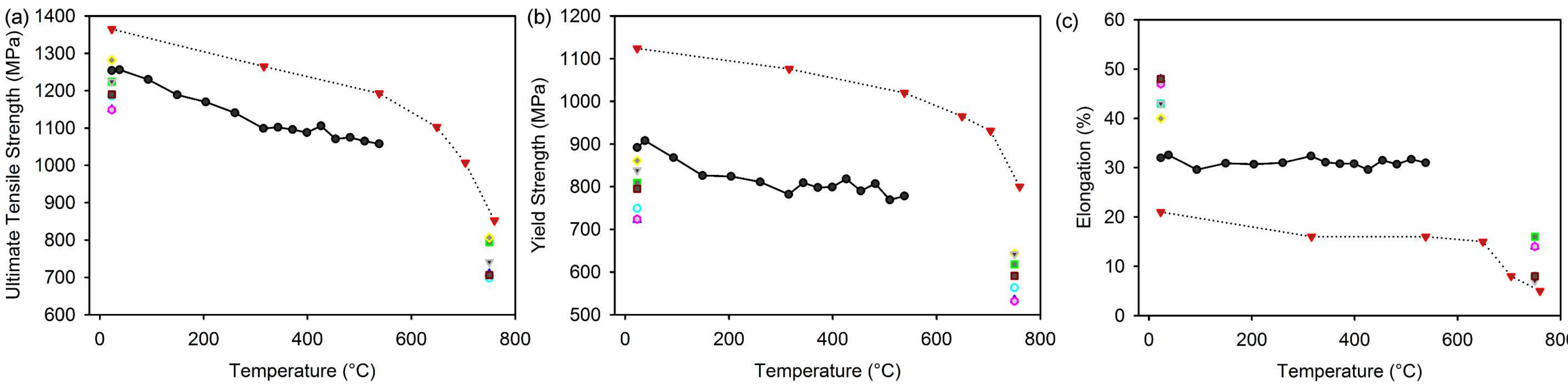
Following Aging

- Equiaxed grain structure of ASTM 6 grain size.
- Stable MC, $M_{23}C_6$ carbides and γ′ precipitates.
- MCs are Nb-carbides (0.1% - 1.5 µm). Partitioning of Ti and Ta.
- Increased presence of $M_{23}C_6$ carbides with decreasing Ti/Al ratio.
- γ′ precipitate size and fraction increased with decreasing Ti/Al ratio.

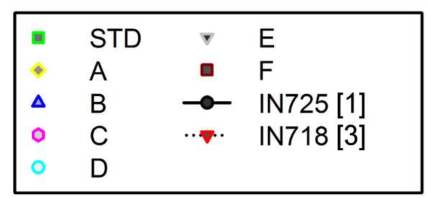


IN725 Mechanical Properties

Tensile Properties

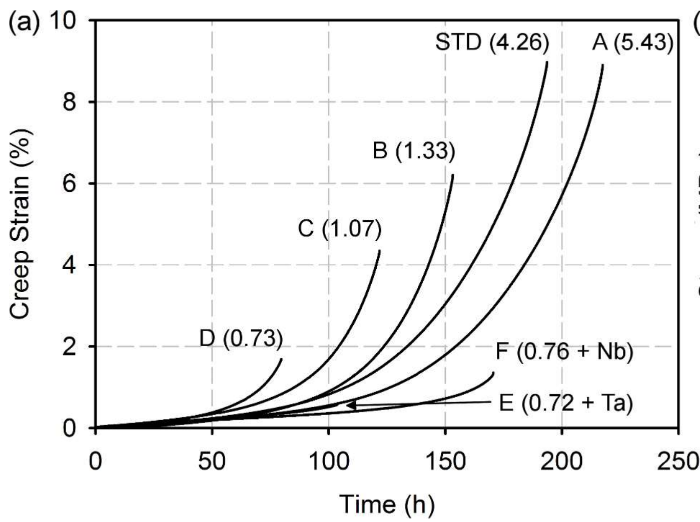


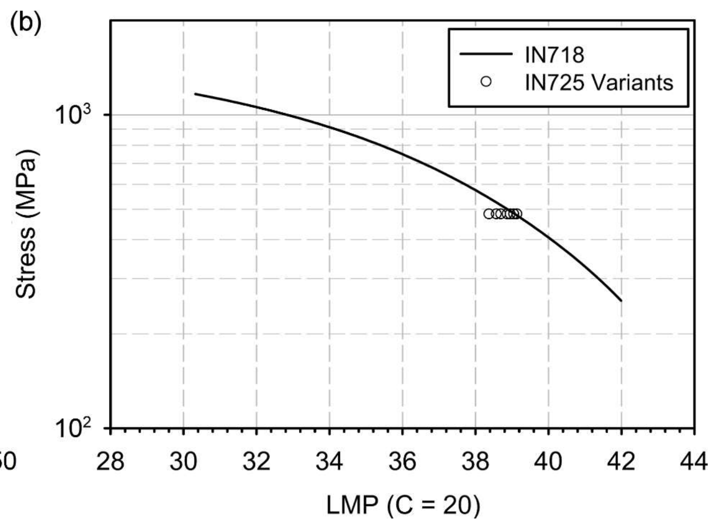
- Comparable to commercial IN725.
- Greater elongation at room temperature.
- Lower strength with decreasing Ti/Al ratio.
- Increases with addition of Nb or Ta.



Mechanical Properties

Creep Properties



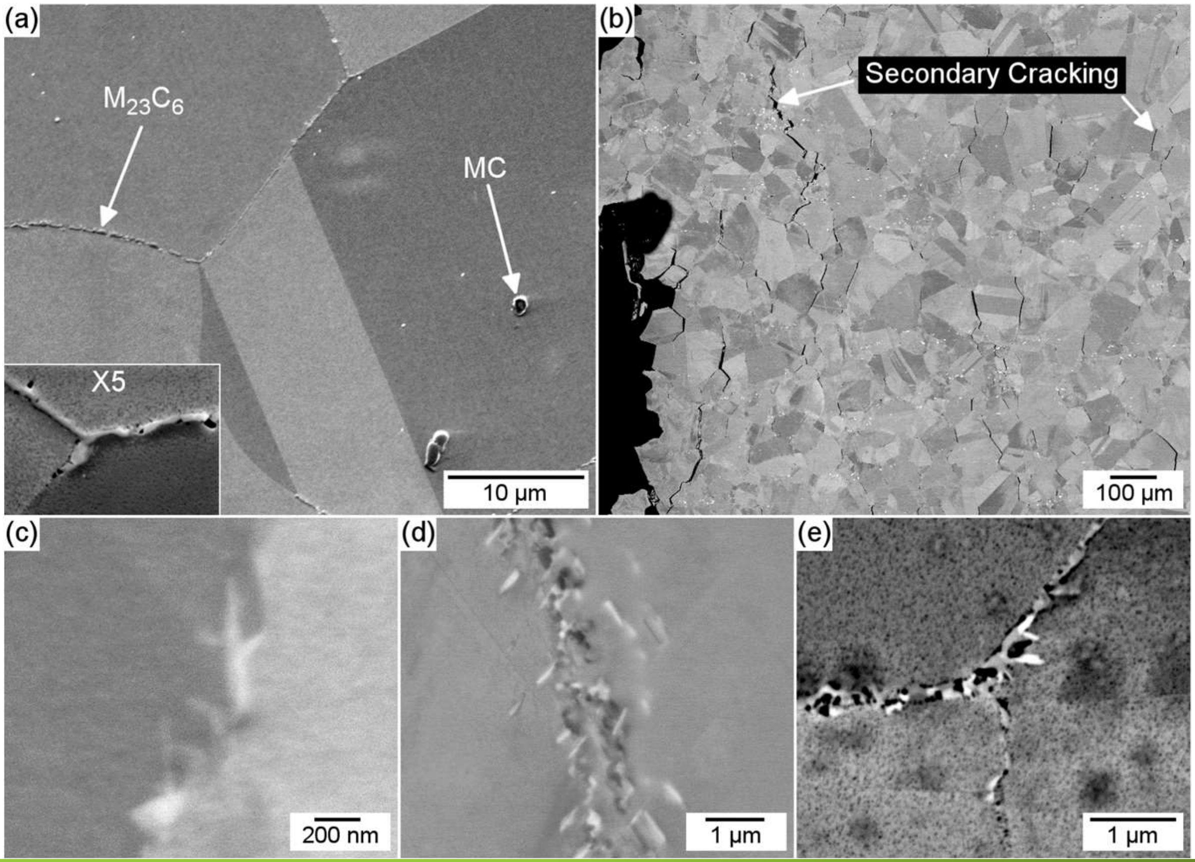


- Decreasing creep strain and time to failure with decreasing Ti/Al ratio.
- Increase in time to failure with addition of Nb or Ta.
- Significant increase in time to failure with addition of Nb.
- Comparable LMP to that of IN718.

Mechanical Testing

Microstructure Following Deformation

- Micrographs following creep testing.
- Larger and denser distribution of the $M_{23}C_6$ carbides following creep testing (a).
- Secondary cracking along the grain boundaries close to the fracture surface (b).
- Decrease in Ti/Al ration and increase in Ta/Nb content resulted in more pronounced secondary cracking.
- Bright phase present in all specimens, identified as δ (c-e).
- Density of the δ phase decreased with decreasing Ti/Al ratio and significantly increased with Nb content (d,e).



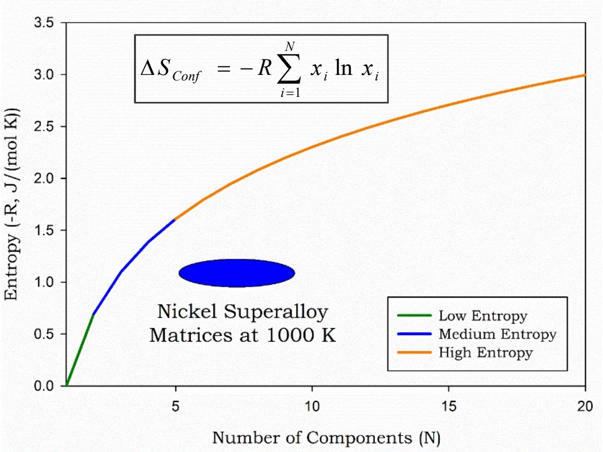
IN725 status

- Low Ti/Al ratio
  - Increased GB carbides increased Gamma Prime and increased secondary cracking: lower creep life
- Additions of Nb and (Ta) raised delta level and reduced gamma/gamma prime mismatch giving longer creep life.
- Differences in database predictions—why we use more than one.
- Work continues…

HEA Alloys for FE Application

A new class of materials?

- HEA alloys have garnered significant interest since Cantor first published his work.
- Will these ever be commercial? Haynes makes several alloys that are not Fe, Co or Ni based such as H120 (FeNiCr), H160 (NiCoCr), H188 (CoNiCrW), and H556 (FeCrNiCo).
- NETL has melted over 31 heats using commercially scalable methods including VIM and ESR with weights from 7 to 50kg. (At a recent presentation at TMS a professor extolled the virtues of his 1.5g button melts.)
- Special attention is required for this class of material in all matters. For example, it has been found that traditional hotworking guidelines may not apply. Once again, it is all about the details.
- NETL is working to understand these materials and explore their potential use in a wide range of FE applications.



HEA1 & HEA2 Chemistries

Total of four additional heats manufactured

HEA	Mn	Cr	Ni	Co	Fe	C	N	O	S	Y
	wt%					ppm				
1A	0.5	22.7	25.9	26	24.9	83	67	14	135	NA
2A	20.3	19.1	21.5	21.7	17.4	68	64	11	136	NA
1C	0.0	22.9	26.4	25.5	25.1	260	60	60	20	NA
2C3	19.6	19.4	21.3	21.5	18.2	274	84	4	13	27

- Homogenization heat treatment was computationally optimized: 1000°C/1 h + 1180°C/3 h +1200°C/5 h – all heats.
- Thermo-mechanical processing was similar for both series except second was TMP hotter resulting in *full solution annealed* condition for HEA1C & HEA2C3.
- HEA2A and HEA2C3 were investigated in tension and creep.

Tensile Testing Results – HEA2A vs. HEA2C3

Tensile Behavior as Function of Temperature

Tensile Mechanical Properties of HEA2A

Temp (K)	0.2% YS (MPa)	UTS (MPa)	Elongation (%)	RA (%)
294	535	725	39	66
523	451	588	29	63
773	437	539	24	43
873	355	475	22	23
973	215	321	14	14
1073	93	155	22	23

Tensile Mechanical Properties of HEA2C3

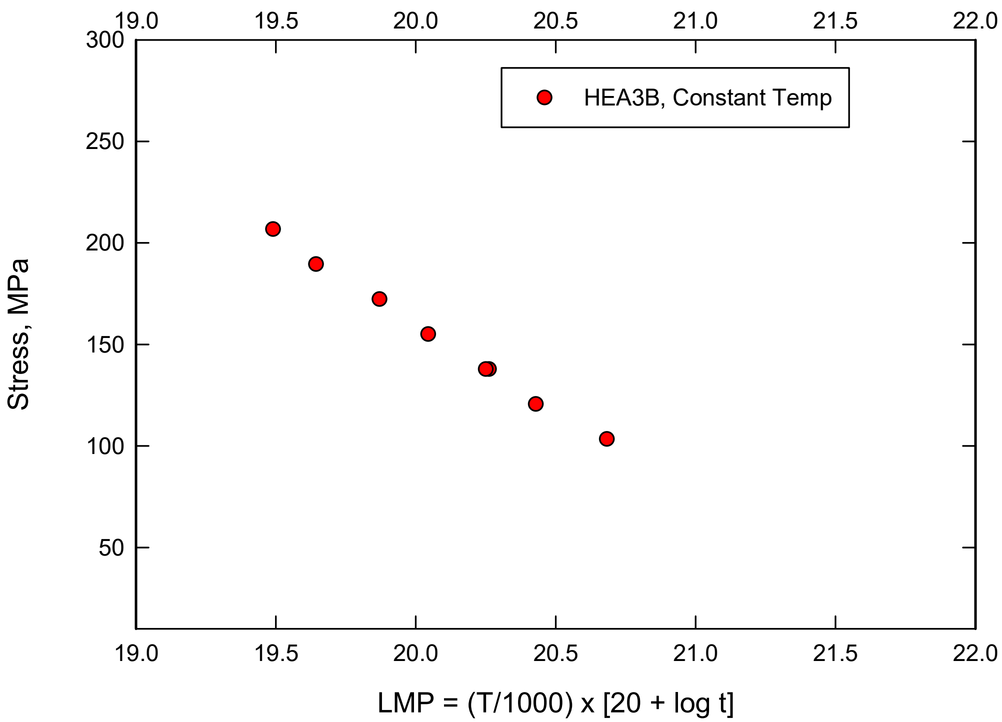
Temp (K)	0.2% YS (MPa)	UTS (MPa)	Elongation (%)	RA (%)
294	238	613	58	79
523	185	511	53	80
773	158	489	53	71
873	150	417	52	49
973	141	292	43	31
1073	120	187	76	54

Change in [YS]/[UTS] as Function of Temperature

ID/TEMP	294K	523K	773K	873K	973K	1073K
HEA2A	0.7379	0.7670	0.8108	0.7474	0.6698	0.6000
HEA2C3	0.3883	0.3620	0.3231	0.3597	0.4829	0.6417

Plot of Stress vs. LMP for HEA3B

103.4 to 206.4 MPa at 600°C (873K) (equivalent to HEA2 with Nb and C)

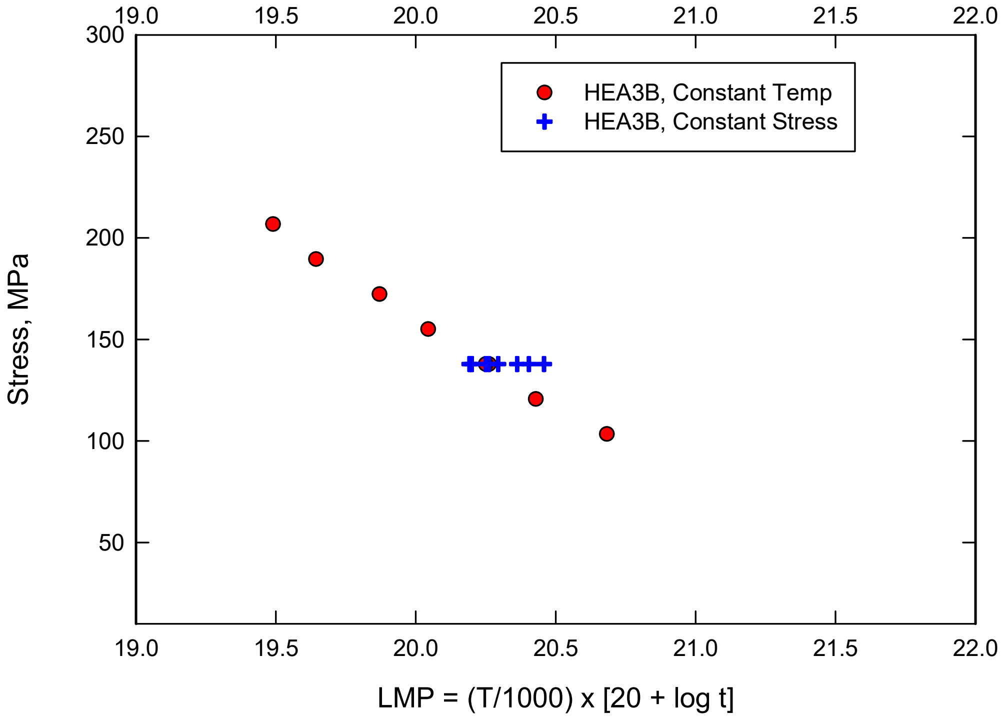


Stress (MPa)	LMP	Time to Failure (hours)
206.8	19.4906	210
189.6	19.6444	315
172.4	19.8706	572
155.1	20.0450	906
137.9	20.2616	1,604
137.9	20.2501	1,556
120.7	20.4292	2,495
103.4	20.6829	4,872

Note the LMP results for the creep screening Conditions for HEA3B (Δ% = 0.06).

Plot of Stress vs. LMP for HEA3B

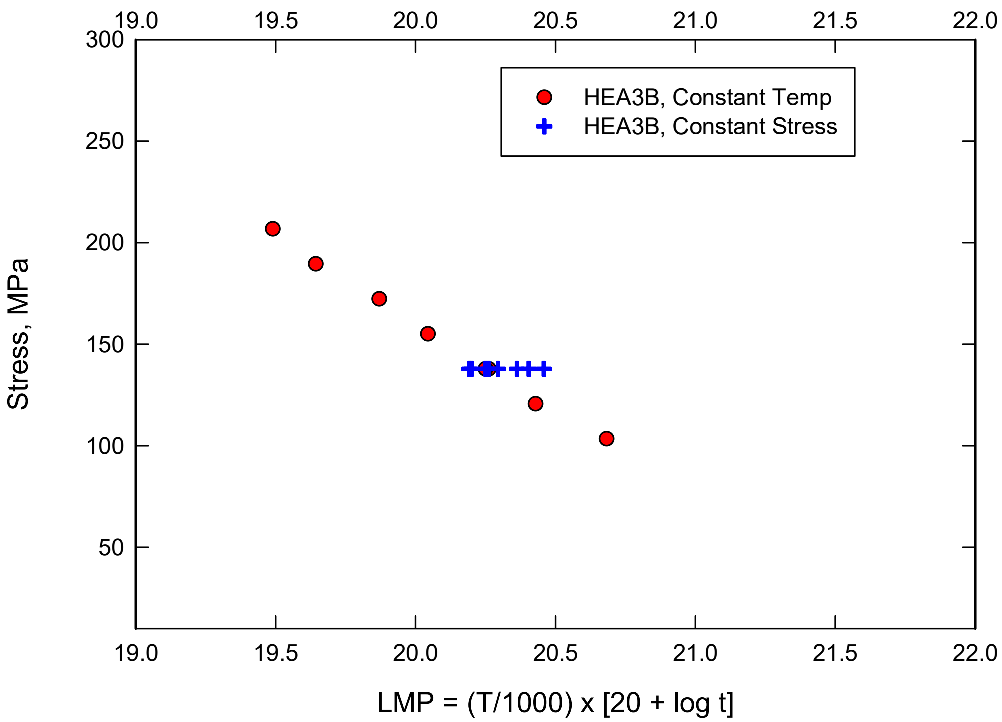
137.9 MPa from 575°C (846K) to 650°C (923K) (equivalent to HEA2 with Nb and C)



Temperature (°C)	LMP	Time to Failure (hours)
650	20.4583	145
637.5	20.4045	255
625	20.3621	469
612.5	20.2946	822
600	20.2616	1,604
600	20.2501	1,556
587.5	20.2004	2,959
575	20.1917	6,408

Plot of Stress vs. LMP for HEA3B

137.9 MPa from 575°C (846K) to 650°C (923K) (equivalent to HEA2 with Nb and C)



At a constant stress, the LMP value should be roughly the same no matter what the temperature of the test or the duration of that test.

For HEA3B the LMP value decreased from a high of 20.4583 for the shortest creep life (145 h) to a low of 20.1917 at the longest creep life (6408 h).

This suggests continuous evolution of the microstructure during the test as evidenced by σ formation in the grip section.

Summary & Conclusions

Current status of Advanced Alloy Development

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- **An advanced ferritic/martensitic steel has been developed and patented which has ~50F advantage over the best commercial alternatives. Several large heats have been made for weldability studies.**
- **An optimized homogenization process was instrumental in improving the creep performance of cast H282. Work continues on developing a secondary option alloy.**
- **Modified versions of IN725 have been manufactured and preliminary evaluations performed.**
- **Commercially scalable manufacturing techniques were used to produce HEA alloys. These alloys appear to have properties similar to austenitic steels although alloy stability in some is questionable.**
- **Throughout all of these efforts we endeavored to employ the following:**
  - Application driven alloy designs.
  - Computational modeling where appropriate.
  - Industrially relevant feed materials.
  - Industrially scalable melting and fabrications techniques.

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