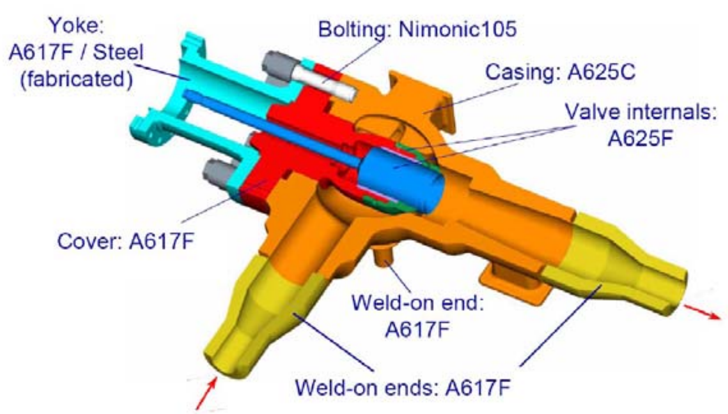
Addressing Materials Processing Issues for A-USC Steam Turbines

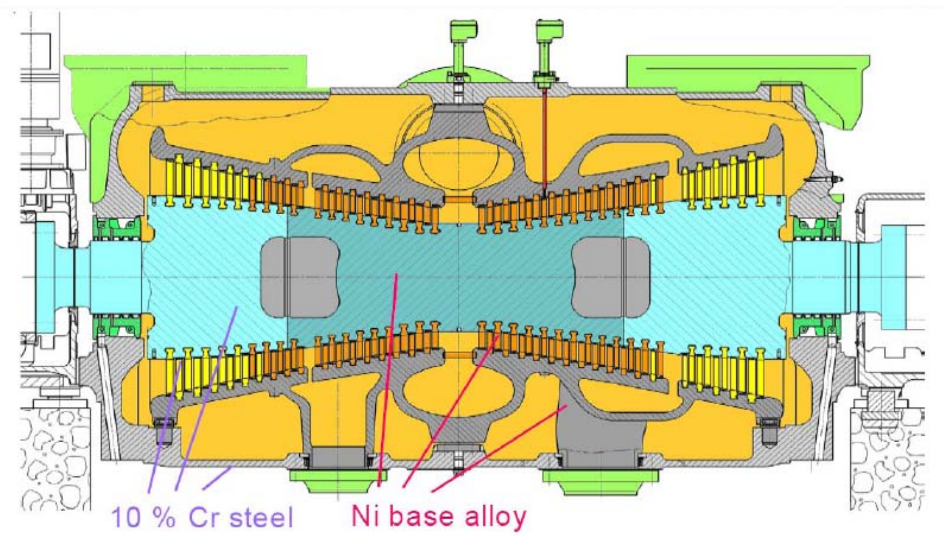
Paul D. Jablonski, Joe Licavoli and Jeffery Hawk

Example Components

- **Castings**
  - 1-15 tons
  - Up to 100mm in thickness



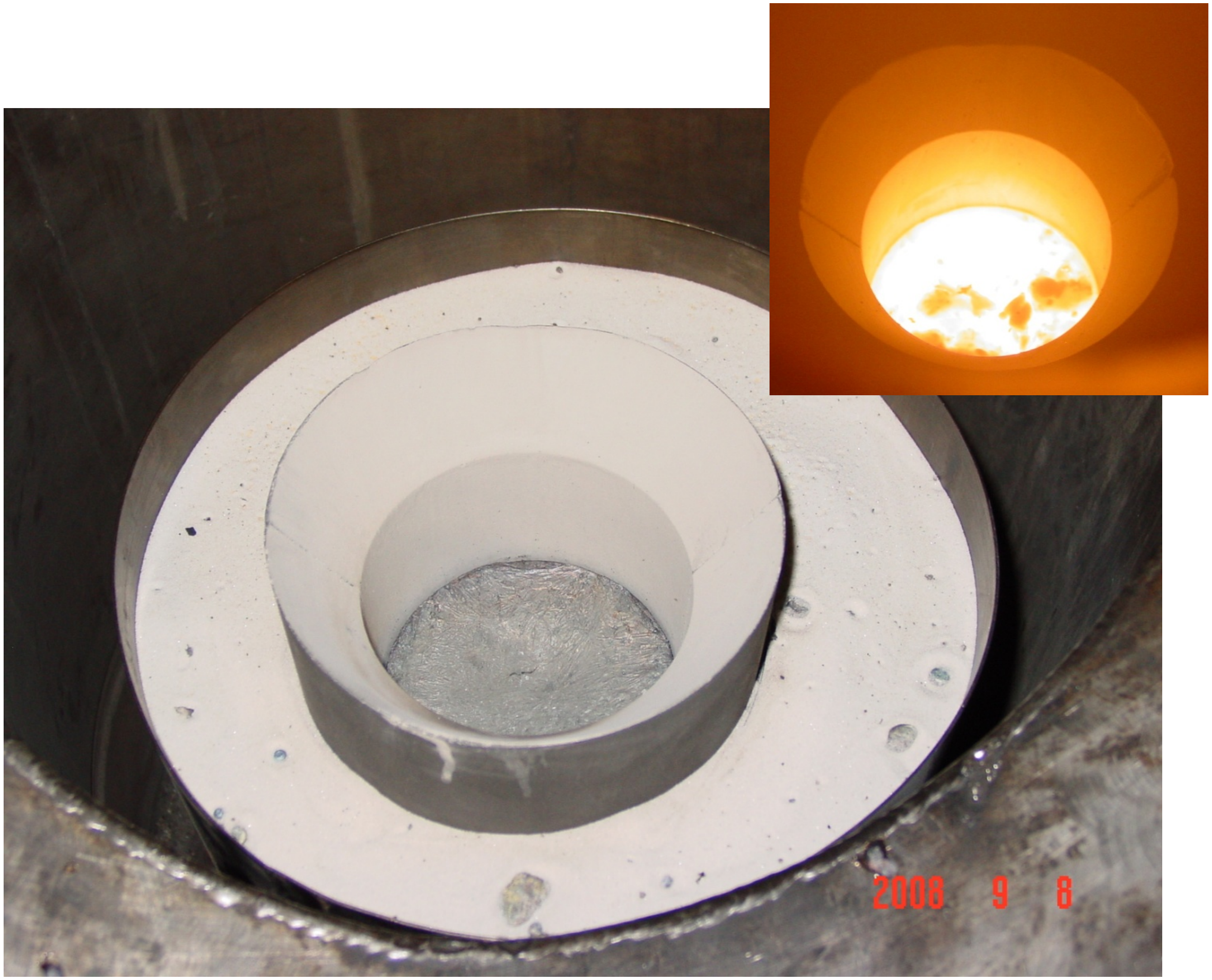
Valve Bodies



Turbine Casing

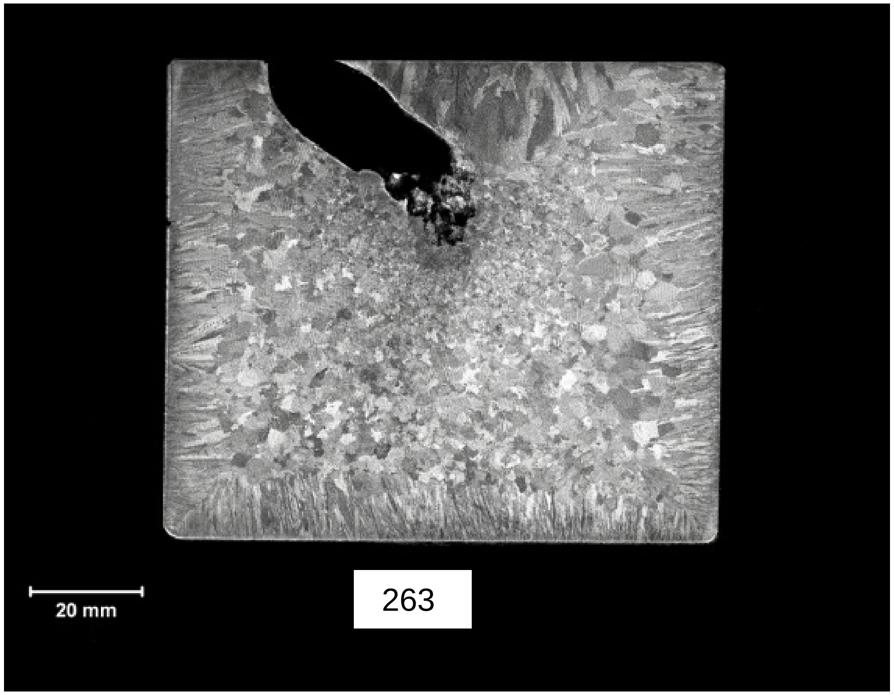
Courtesy Alstom

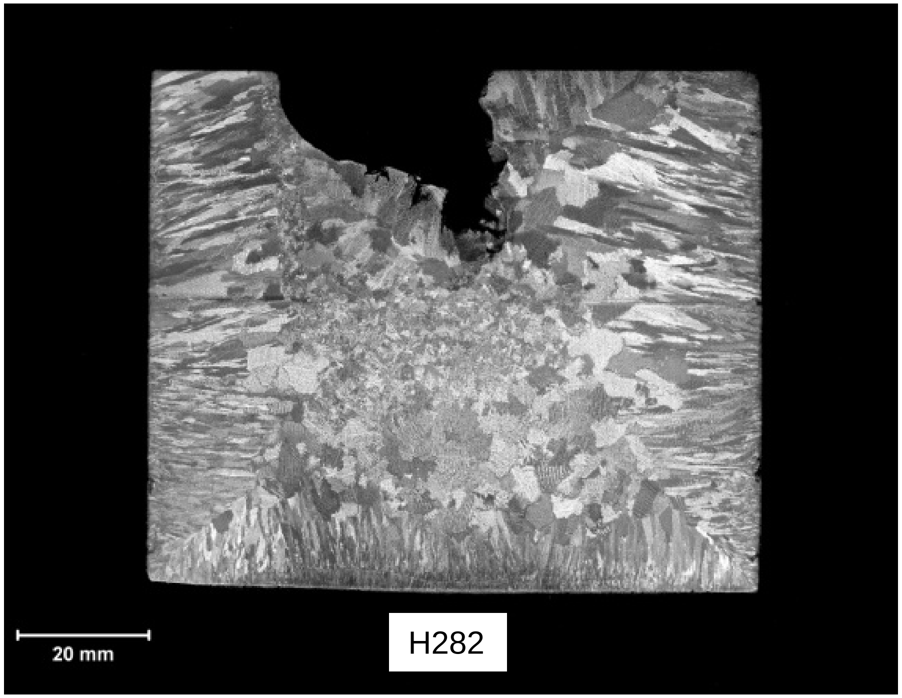
Initial Trials With Small Scale Casting



When the ingot was cast the mold never showed any "color" which meant that the mold temperature stayed below about 550C. This gave us some confidence that slow cooling was achieved.

Grain Etched Ingot Cross Sections



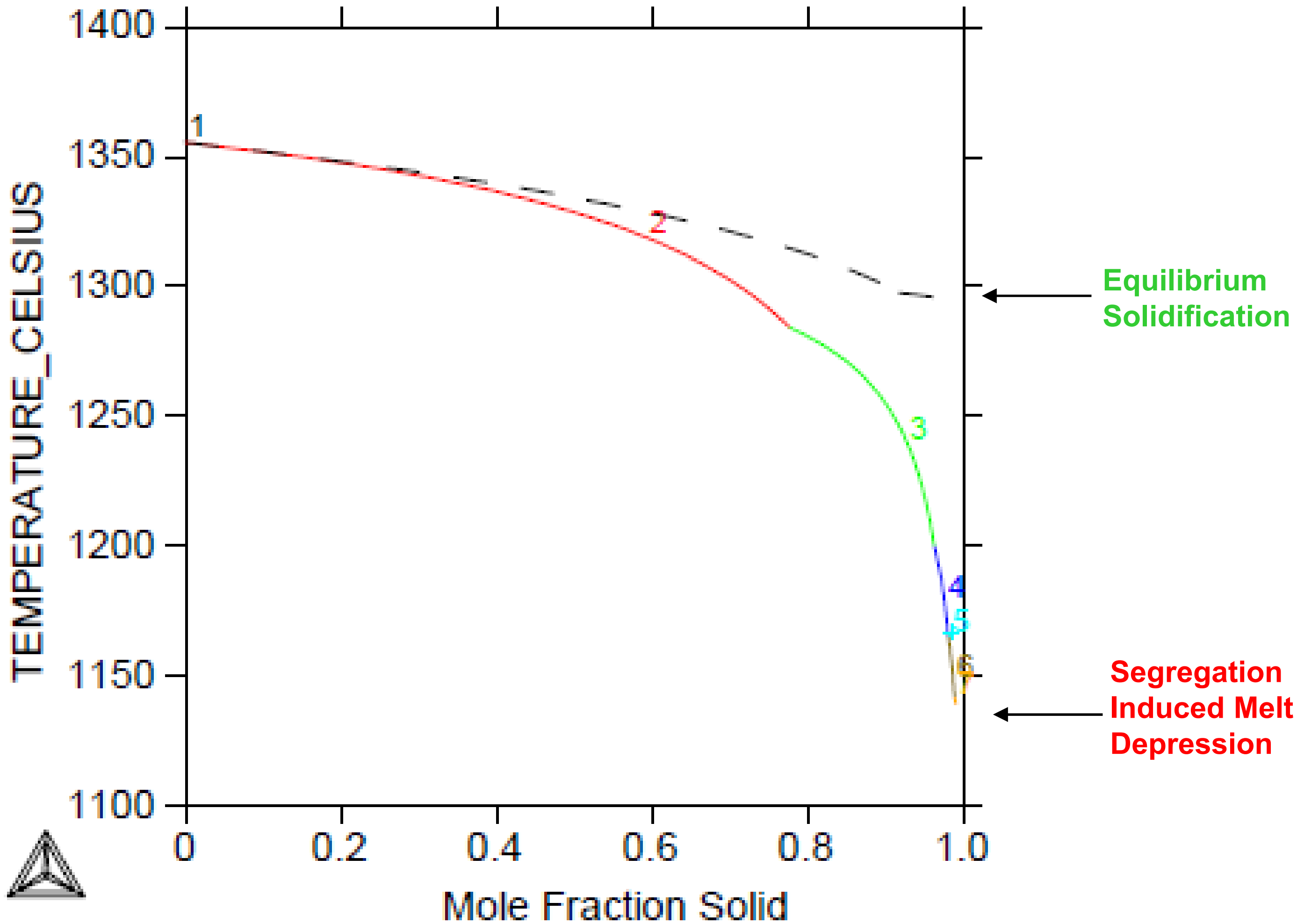


Ingots were sectioned to bisect the shrink cavity.

In general, the ingots have a columnar outer band ~1/4-1/3 of the radius thick and an equiaxed core. This is similar to the grain structure we would expect to observe in a large sand cast version of these alloys.

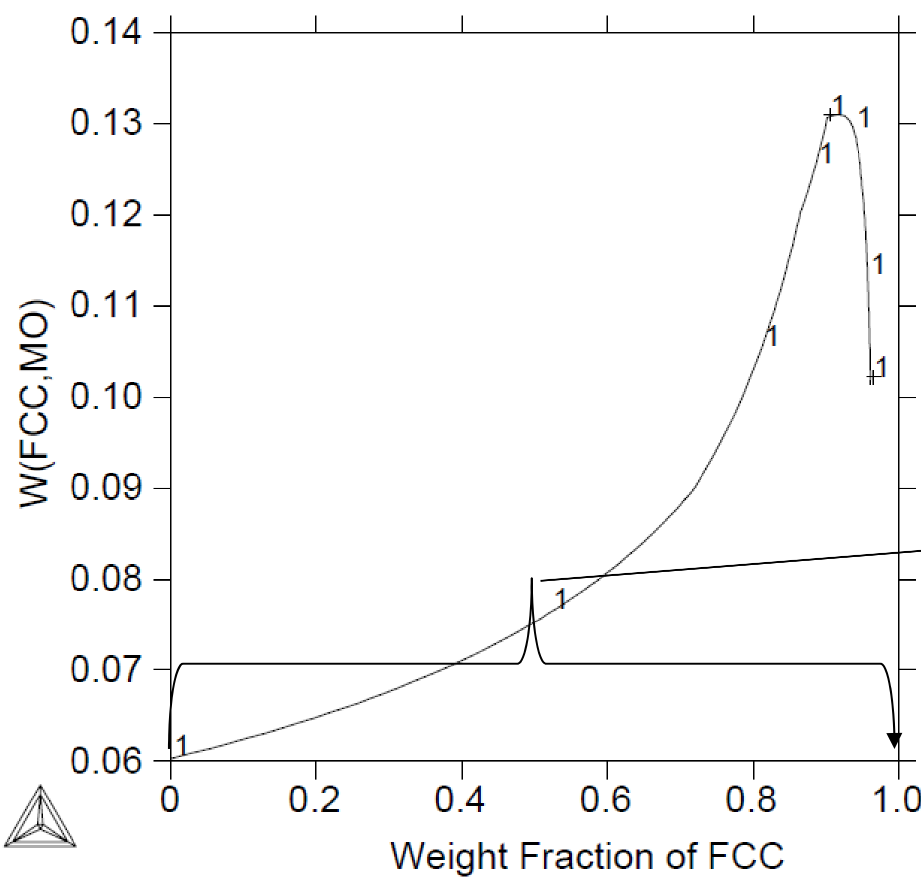
SDAS: ~45-65 µm in columnar; ~80-90 µm in equiaxed

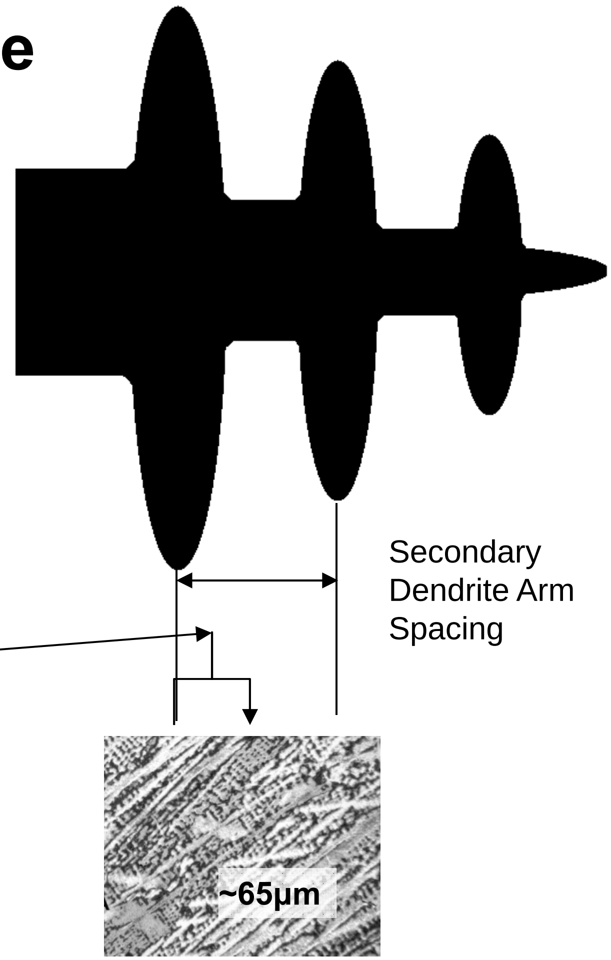
263—Solidification



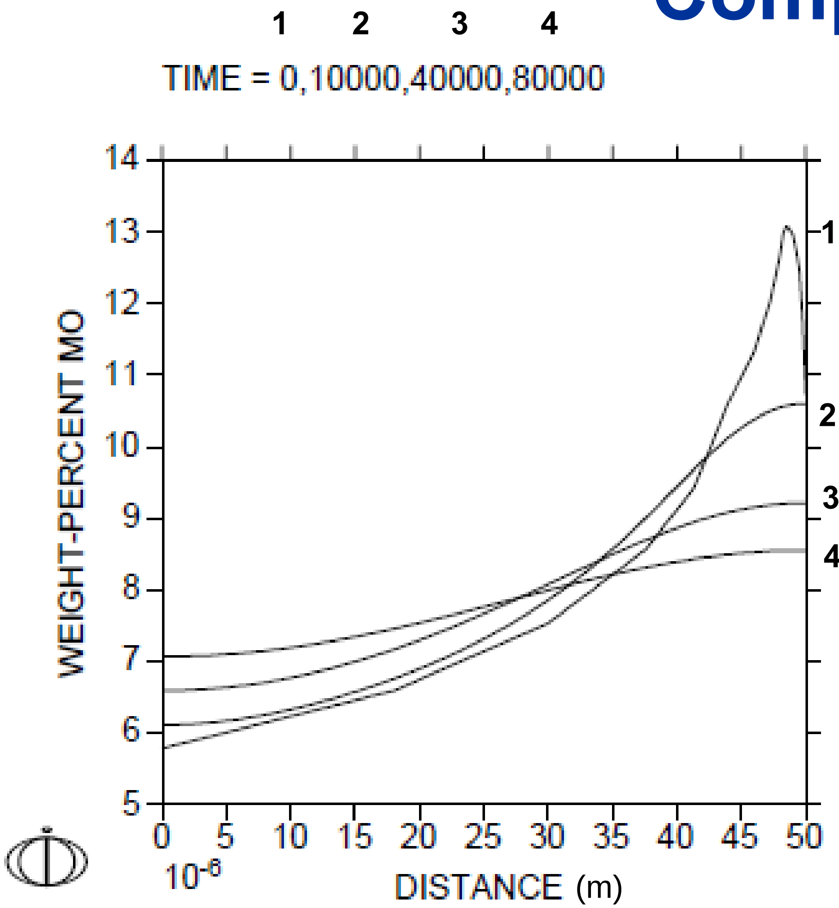
Variation of Mo in the FCC Phase

Segregation Within the FCC Phase

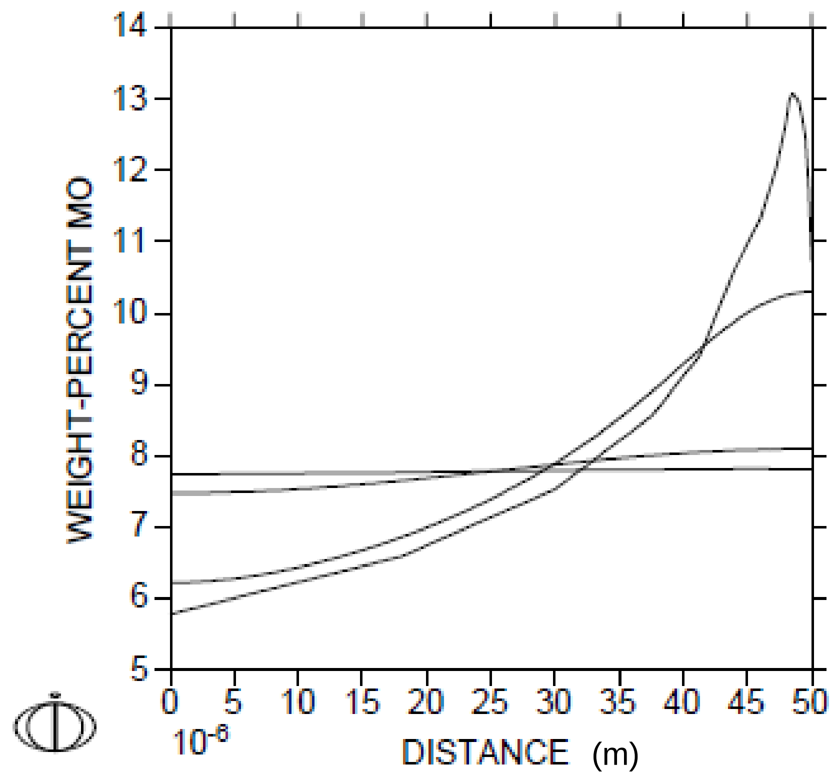




H282—Homogenization Heat Treatment Comparison



Isothermal at 1100C

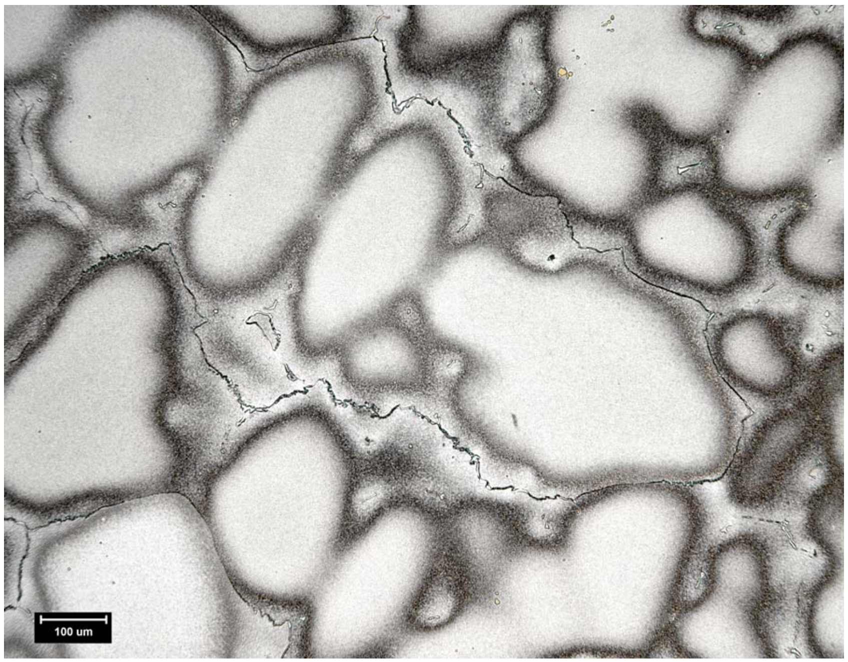


1100C/10,000s+1200C/remaining time

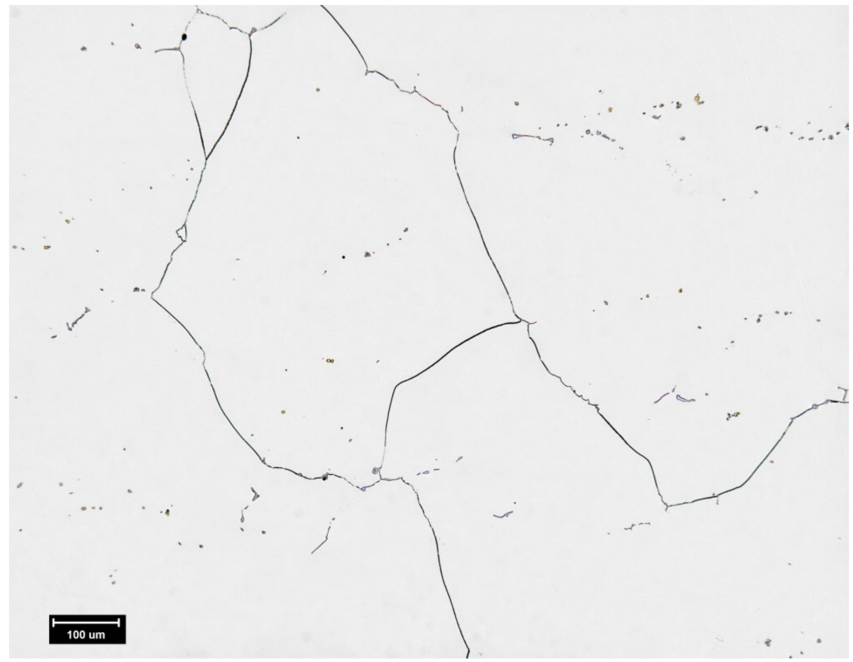
Patent Pending
*Metall. Trans. B, **40B**, (2009) 182.*

As-Cast vs. Homogenized H282

Qualitative Confirmation of the Effectiveness of the Homogenization Heat Treatment

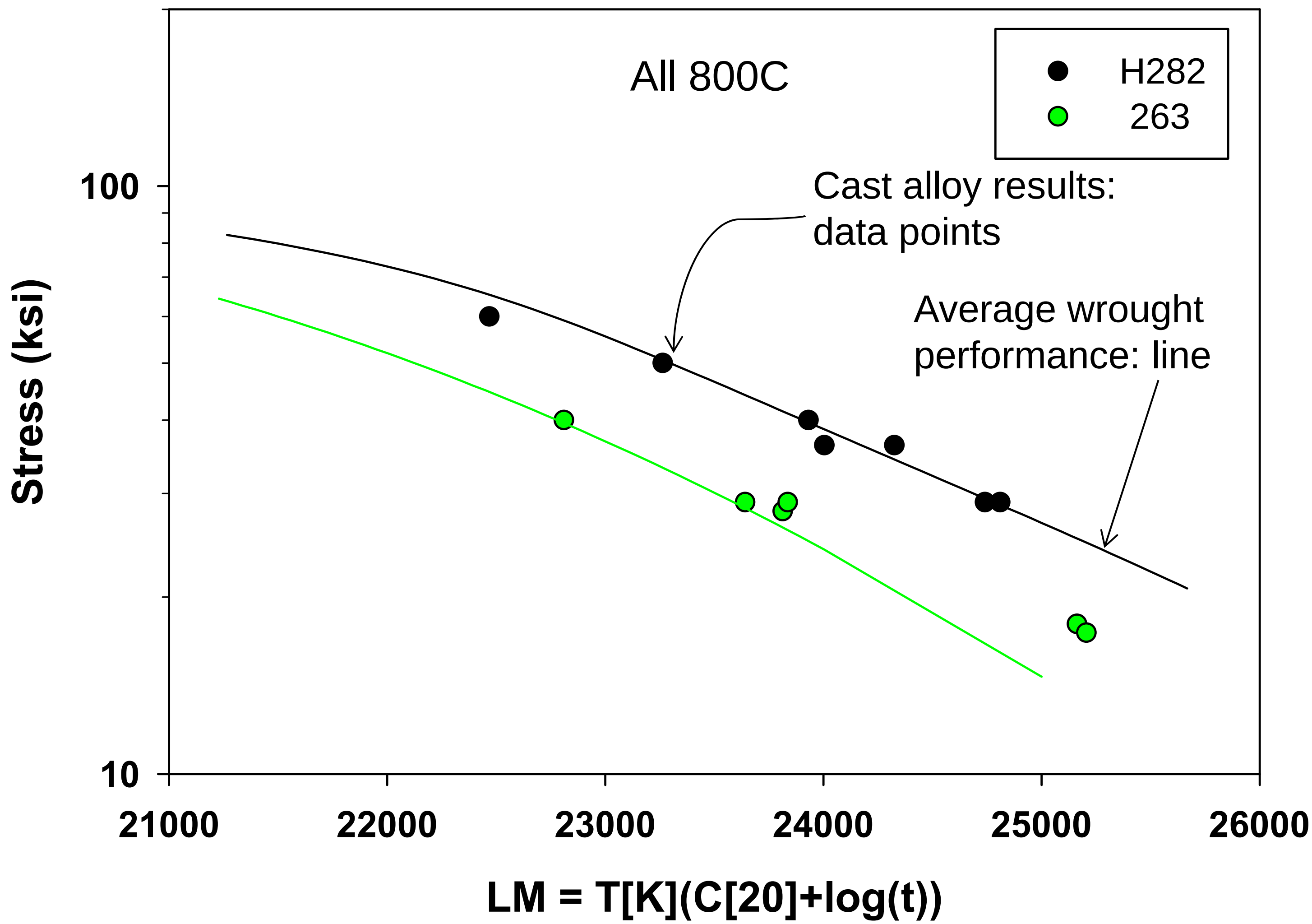


As-Cast

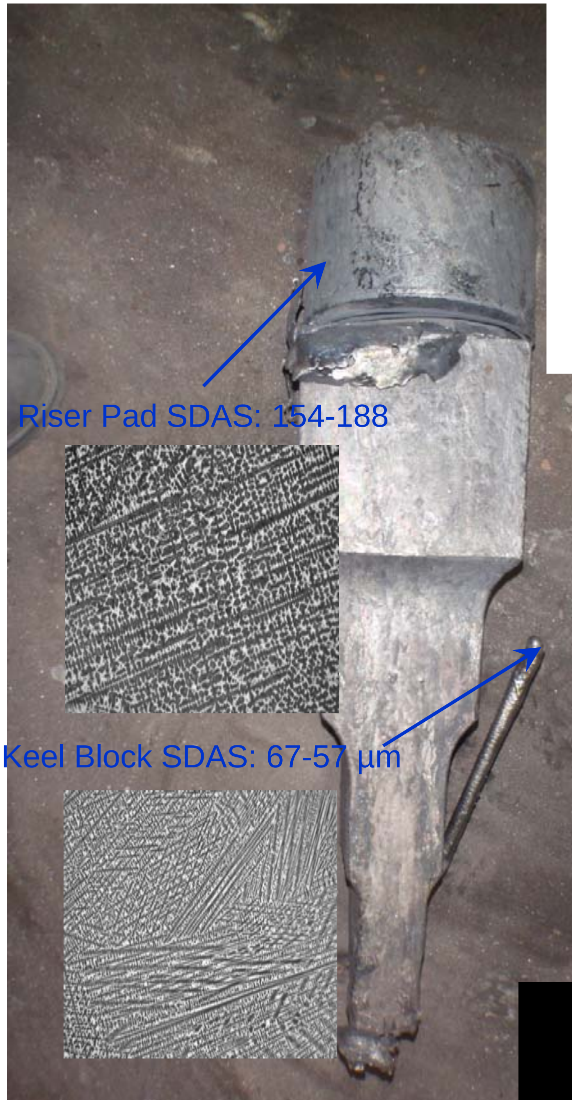


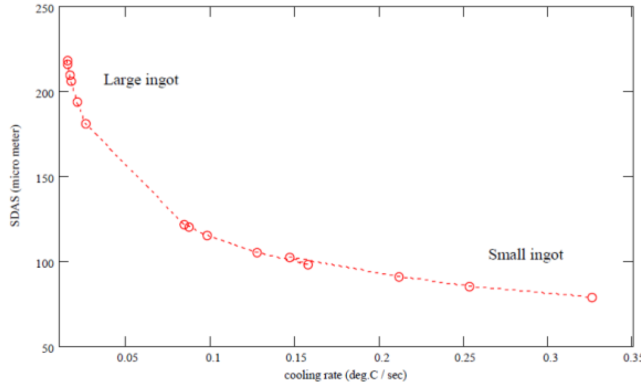
Homogenized

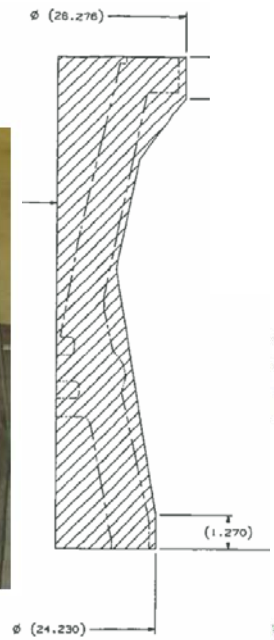
Comparison to Wrought Properties



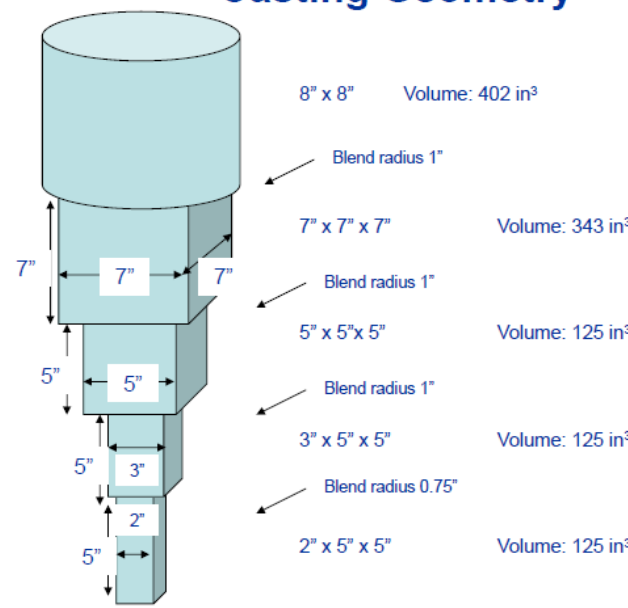
Trial Castings

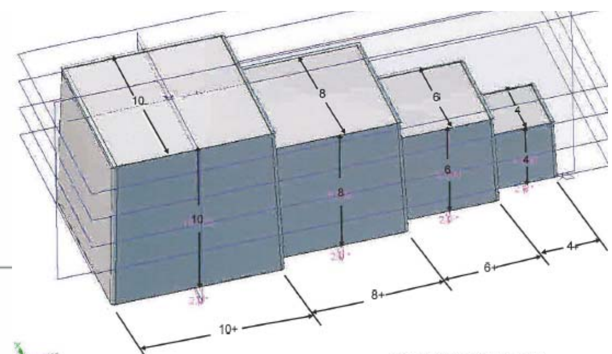




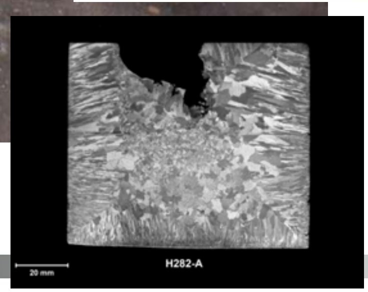


Casting Geometry





STEP BLOCK TEST PATTERN
ADD 2 DEG. DRAFT & 3/8" SHRINK RULE

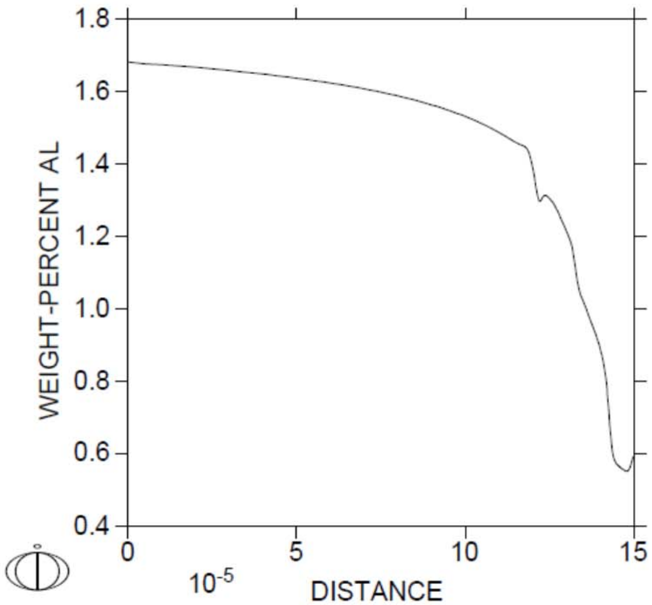


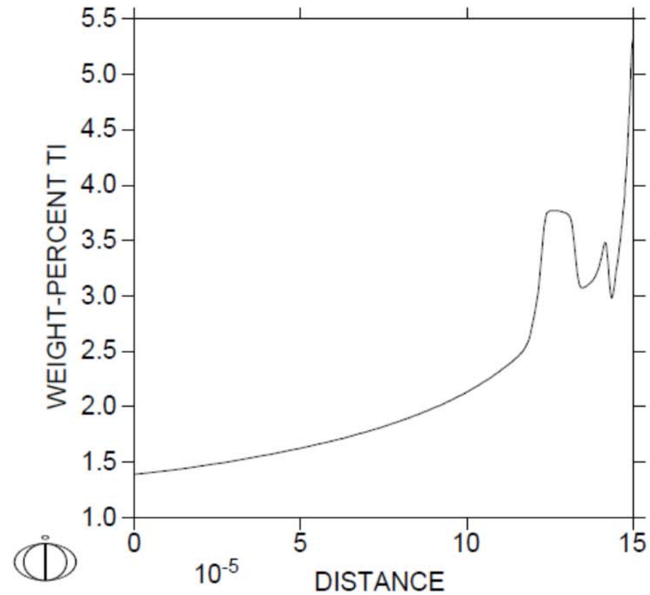
LABORATORY

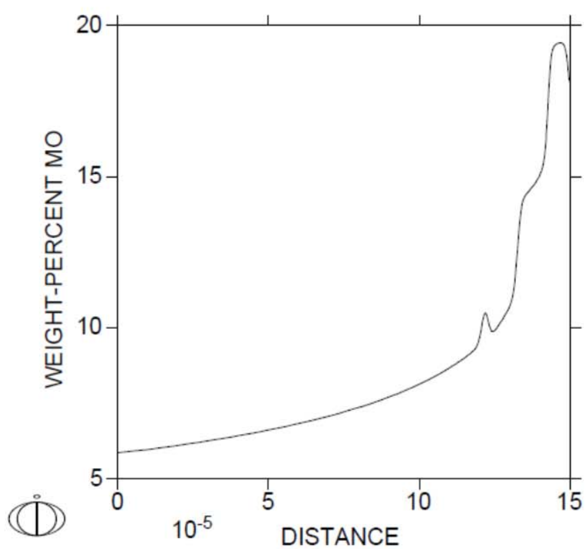
Homogenizing Haynes 282 Steam Turbine Partial Valve Casing Casting

18,500 lb

Variation of Key Elements







Homogenization Proposal 1

Based on a SDAS of 300 microns.

The first calculations were made aiming for a temperature 50C below the incipient melt point (IMP) which we maintained except for a couple of instances.

Temp (C)	Time (h)	IMP-T (C)
1115	3	54.4
1165	3	50.6
1175	3	51.2
1190	8	47.9
1205	12	50.6
1220	24	47.0
1225	24	50.1
Overall	77	

Resulting chemical variation (percent of nominal; all within specification):

	tip	core
Al	98.54%	101.41%
Co	99.57%	100.48%
Cr	99.72%	100.31%
Fe	97.94%	102.10%
Mn	106.54%	93.41%
Mo	105.74%	94.32%
Si	97.01%	102.90%
Ti	97.92%	101.94%

Homogenization Proposal 2

Based on a SDAS of 300 microns.

The second calculations were made aiming for a temperature 40C below the incipient melt point (IMP) which we were able to maintain throughout.

T(C)	t(h)	IMP – T (C)
1125	3	44.4
1175	3	42.2
1185	3	43.7
1200	6	40.8
1215	6	40.4
1220	6	43.2
1225	6	43.4
1230	12	41.5
1235	18	40.1
Overall	63	

Resulting chemical variation (percent of nominal; all within specification):

	tip	core
Al	98.36%	101.58%
Co	99.47%	100.60%
Cr	99.60%	100.45%
Fe	97.59%	102.45%
Mn	107.44%	92.50%
Mo	106.59%	93.50%
Si	96.92%	102.95%
Ti	97.92%	101.89%

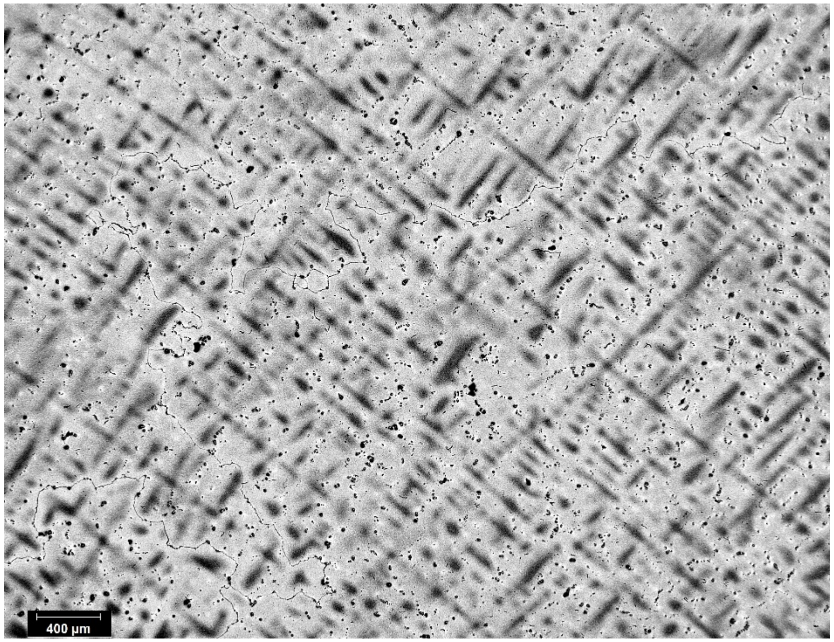
Homogenization of Large H282 Castings

ESR Ingot

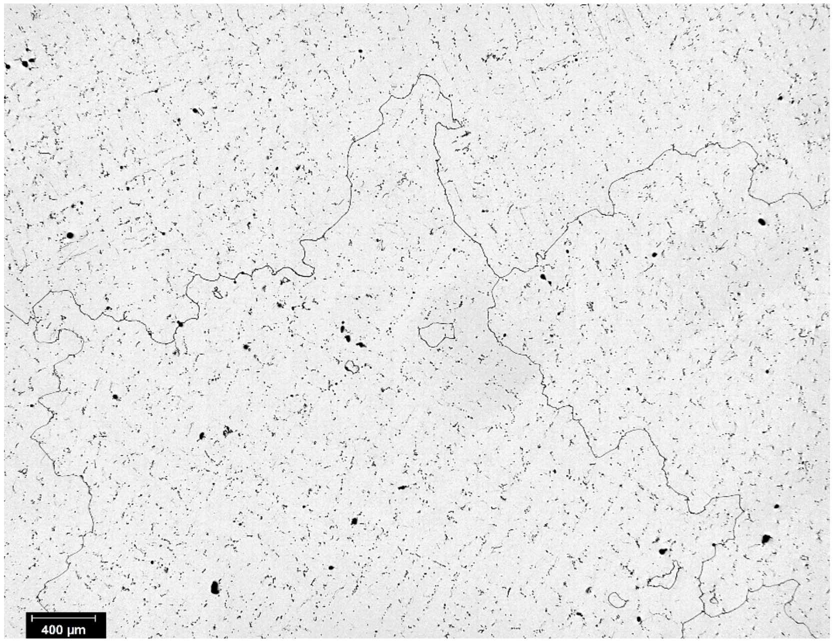
VAR Ingot: 24in Diameter x 71in long, ~10,000lb

- Small ingots (15#): 1100C/3h + 1200C/9h (100µm)
- Metaltek (300#): 1130C/3h + 1200C/3h + 1210C/14h (150µm)
- Flowserve (1000#): 1100C/6h + 1200C/48h (200µm)
- Special Metals (10,000#): 1133C/4h + 1190C/8h + 1223C/30h (200µm)

Partial Valve Casing Casting Microstructure



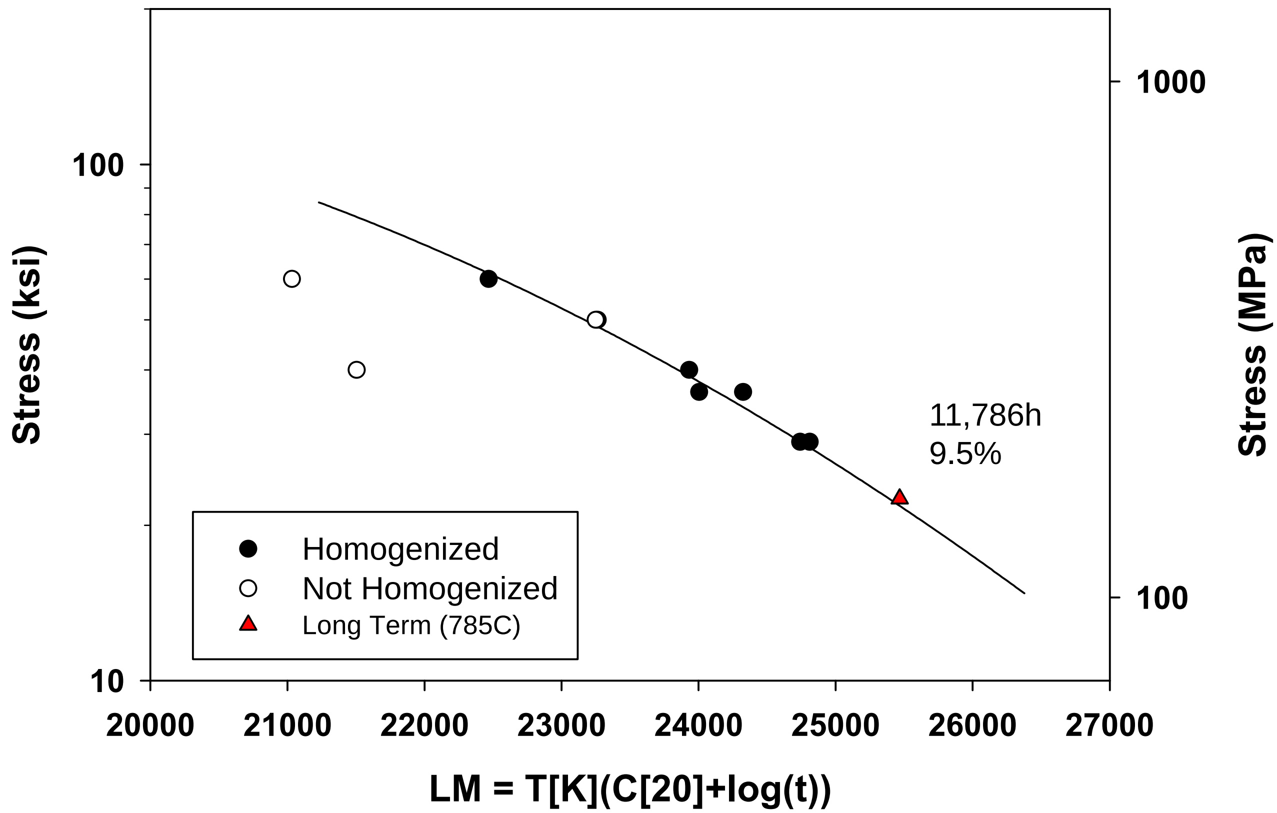
As-Cast



Homogenized

1115C/3h + 1165C/3h + 1175C/3h + 1190C/8h + 1205C/12h + 1220C/24h + 1225C/24h

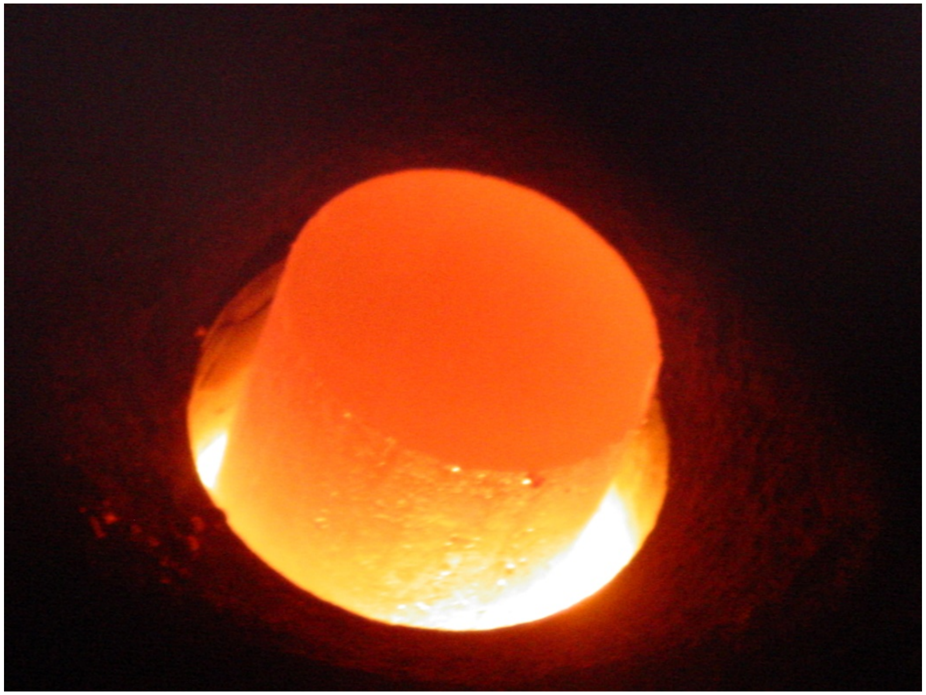
Cast H282



Stress (ksi)
Stress (MPa)
100
10
1000
100
20000
21000
22000
23000
24000
25000
26000
27000
LM = T[K](C[20]+log(t))
11,786h
9.5%
Homogenized
Not Homogenized
Long Term (785C)

Section Summary

- If new plants operate under A-USC conditions enhanced efficiency and reduced pollution are anticipated.
- Small scale castings were made to evaluate the performance of cast forms of traditionally wrought Ni-based superalloys.
- A computationally optimized homogenization heat treatment was developed to improve the performance of these materials, especially H282.
- Verification of the effectiveness of the homogenization cycles on H282 and alloy 263 have been performed on large scale castings and performance has been verified.



The Practical Application of Minor Element Control in Small Scale Melts

Paul D. Jablonski, Joe Licavoli and Jeffrey A. Hawk

Resulting Chemistries From Vacuum Distillation Trials

Experiment	Cr (w/o)	S (ppm)	C (ppm)	O (ppm)	N (ppm)
50°C/20 min	21.74	50	28	45	61
50°C/20 min	21.74	43	43	173	46
150°C/20 min	21.57	43	<10	59	27
100°C/60 min	21.67	43	16	90	12
100°C/20 min	21.67	39	12	38	17
100°C/10 min	21.63	41	18	42	22

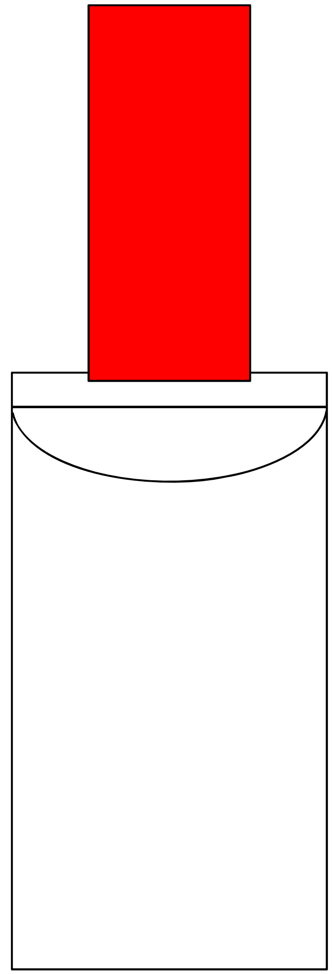
Results of S Gettering Trials

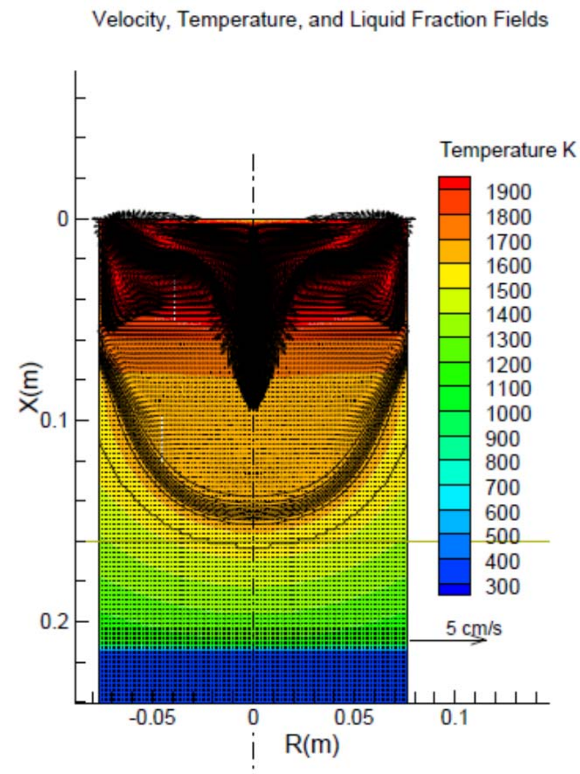
Scoping experiments have been performed to reduce the S level in Ni-based alloys. These experiments included the addition of La, Y, or Mg in addition to the use of vacuum. The results showed good S reduction with La additions.

Experiment	S (ppm)	Other (ppm)
Ni-22Cr		
2.0 g Mg	54	10 Mg
25.6 g IncoMg 1	59	110 Mg
2.0 g Mg in ea. Cr	31	18 Mg
26.5 g NiCrLa	4	102 La
7.1 g Y	23	247 Y
23.3 g NiCrY	14	246 Y
Ni-30Cr		
35.1 g NiCrLa	5	106 La
Ni-40Cr		
46.2 g NiCrLa	33	106 La
Ni-50Cr		
35.1 g NiCrLa	9	227 La
25.4 g NiCrLa	67	61 La
35.1 g NiCrLa	7	118 La

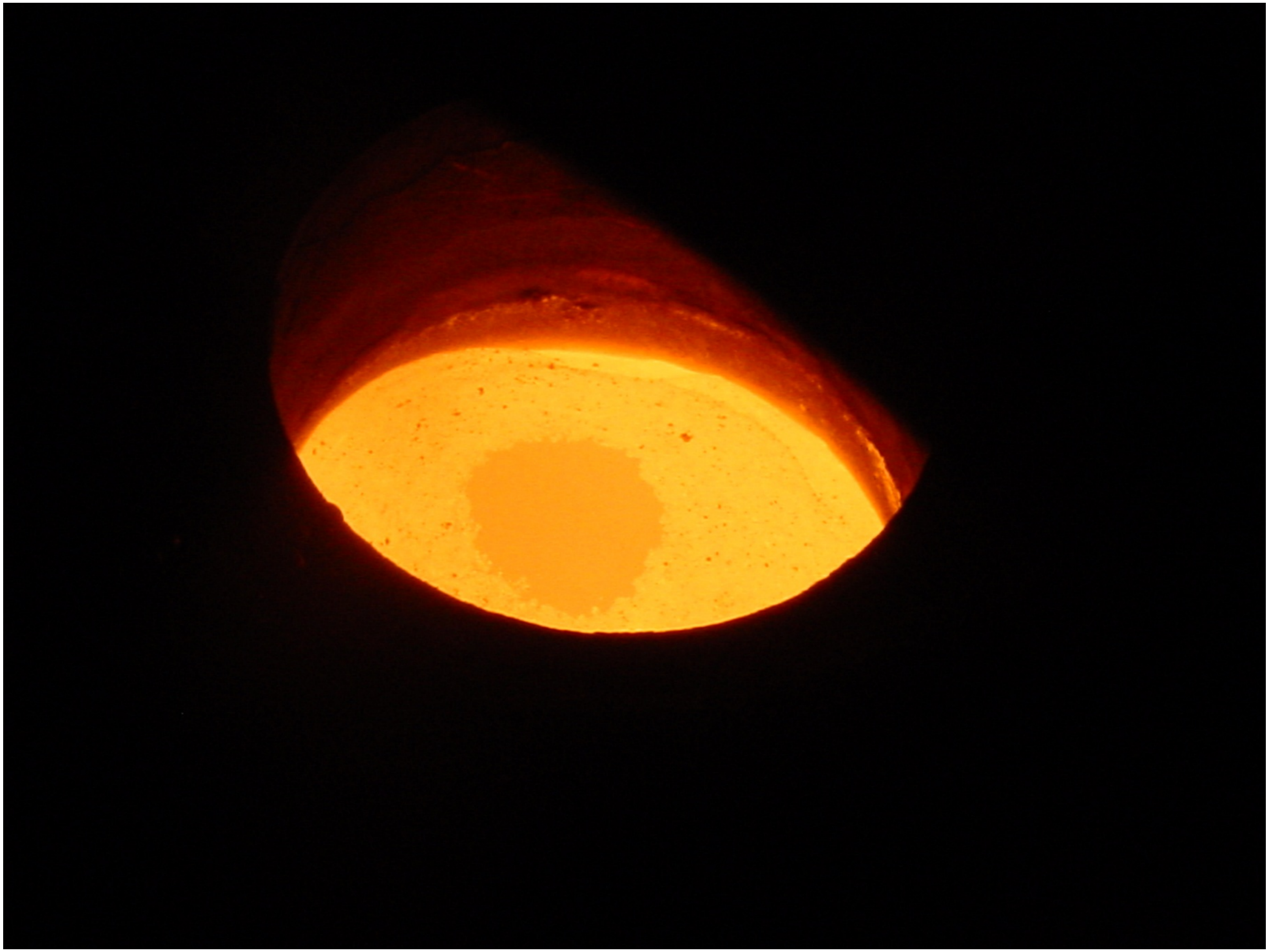
Sulfur Reduction by ESR Melting

- **Ni 30Co 30Cr:**
  - Electrode: 48 ppm
  - Ingot: 12 ppm
- **Ni 30Co 30Cr:**
  - Electrode: 50 ppm
  - Ingot: 14 ppm
- **Ni 50Cr:**
  - Electrode: 54 ppm
  - Ingot: 22 ppm





Reducing S in Ni alloys



Reducing S in Ni alloys

- **It does not seem to be possible (yet) to reduce S below about 50ppm by vacuum distillation.**
  - Very effective in reducing C to very low levels…but if C levels are very high it can make a mess of the furnace.
- **Vacuum levels and leak rates have been significantly improved.**
  - Ultimate vacuum is usually less than 0.1 microns.
  - Leak rates of 0-0.1 microns/minute are typical.
- **Sulfur reduction to ~10ppm or lower has been achieved with addition of reactive metals.**
  - Variable results
  - High level of effort
- **Sulfur reduction via ESR has been successful**
- **Critical component for RE or ESR removal of S is the O level**

- **Subtask 3.2 Superalloy Design & Development**
  - Fireside Corrosion with respect to Mo levels
  - Steam oxidation as a function of pressure
  - Co-authors
    - Gordon R. Holcomb
    - Casey Carney (NETL and AECOM)

Fireside Corrosion

- **Comparison of air-fired and oxy-fired (hot gas recycle case) conditions to examine**
  - The effects of temperature (650 to 800°C)
  - Alkali sulfate flux to the alloy surface
  - **Mo content in Ni-22Cr alloys**
  - NETL developed alloy CPJ7B in comparison to T92
- **Flue gas compositions**
  - Air-firing: N_2-14CO_2-9H_2O-2.5O_2-0.3SO_2
  - Oxy-firing: CO_2-8N_2-20H_2O-2.5O_2-0.9SO_2 (hot gas recycle)
  - Simplified from earlier research, as flue gas compositions were not found to change overall corrosion rates (at 700°C)

Alloys and Ash Compositions (wt%)

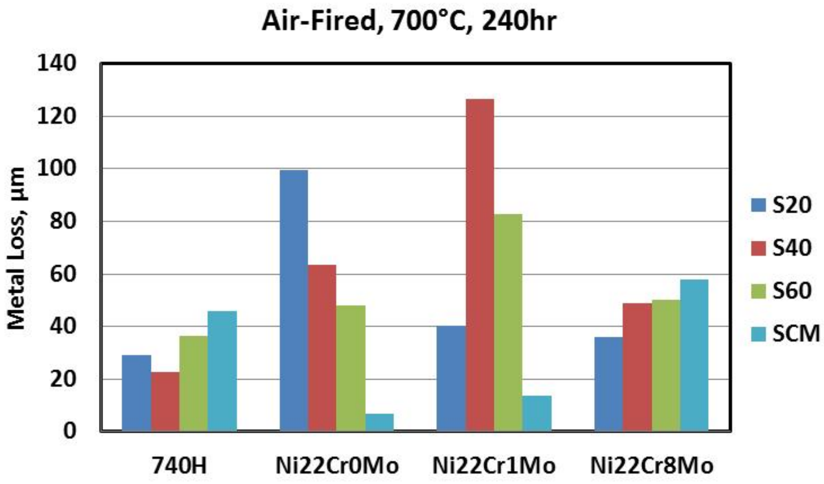
Alloy	Fe	Cr	Ni	Co	Mo	C	Si	Ti	Al	Mn	V	Nb+Ta	Cu	Other
T92	Bal	9.08	0.25	0.01	0.45	0.081	0.09		0.01	0.40	0.21	0.07		1.80 W
CPJ7B In Dev	Bal	9.83	0.27	1.48	1.26	0.15	0.09	0.004	< 0.02	0.41	0.21	0.336	0.03	0.48
740H Nom.	0.7	25	Bal	20	0.5		0.15	1.35	1.35	0.3		1.5		
Ni22Cr 0Mo*		22.18	Bal		0.02	0.043		0.01	0.08			0.01	0.01	11 ppm S
Ni22Cr 1Mo*		22.04	Bal		0.99	0.050			0.07			0.02	0.01	4 ppm S
Ni22Cr 8Mo*		22.04	Bal		7.77	0.052			0.07			0.01		11 ppm S

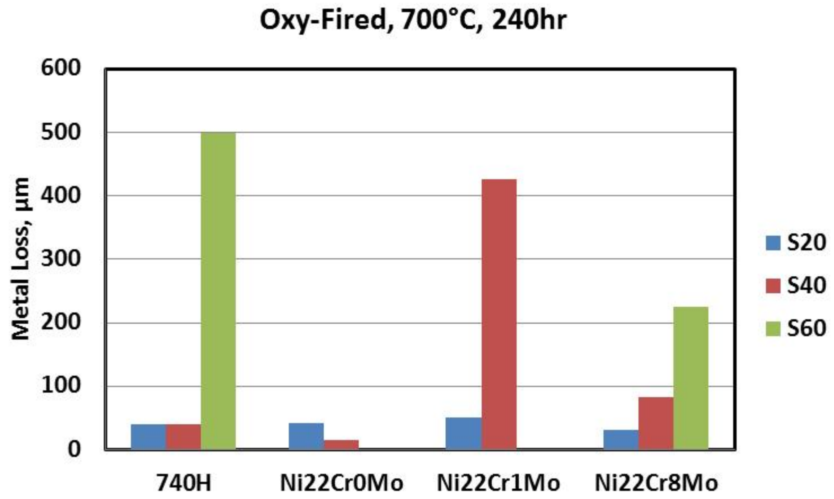
Ash Compositions

- Maintain 3:1 ratio of $(Na,K)_2SO_4$:Fe_2O_3 as found in lowest melting point alkali iron trisulfates
- Different alkali sulfate fluxes to alloy surfaces

ID	Al_2O_3	SiO_2	Fe_2O_3	Na_2SO_4	K_2SO_4
SCM	0	0	25	37.5	37.5
S80	10	10	20	30	30
S60	20	20	15	22.5	22.5
S40	30	30	10	15	15
S20	40	40	5	7.5	7.5

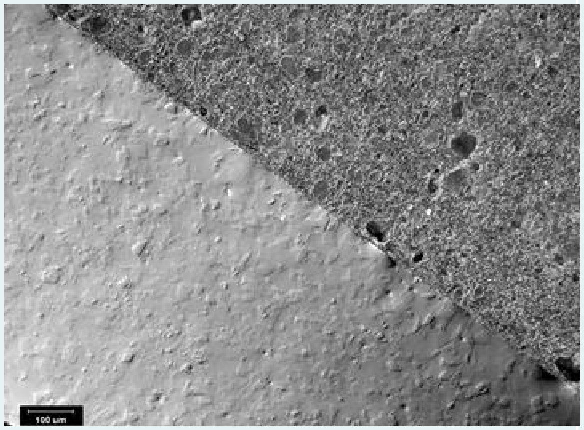
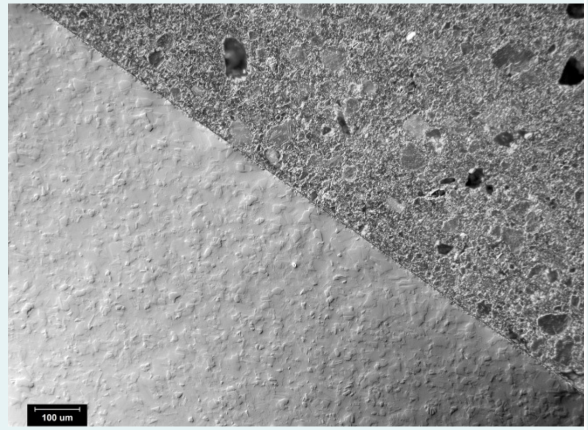
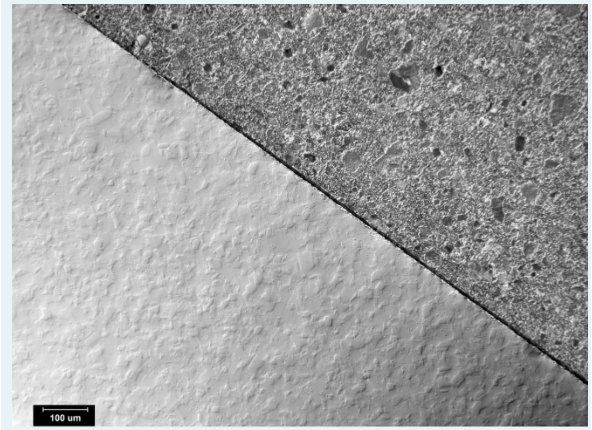
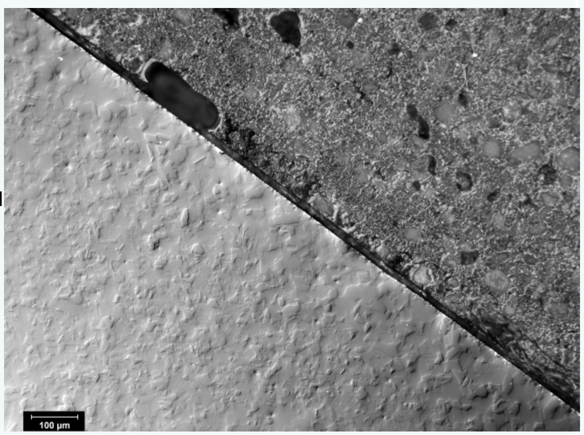
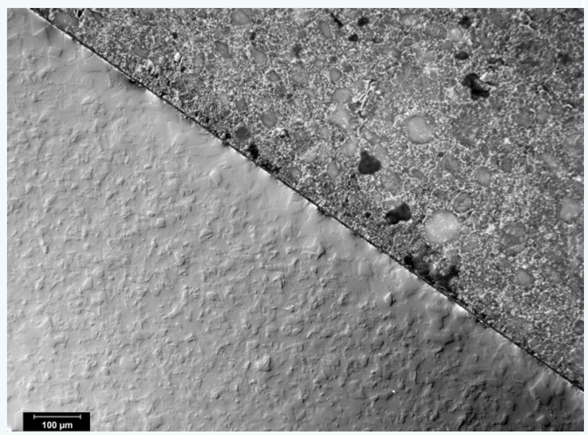
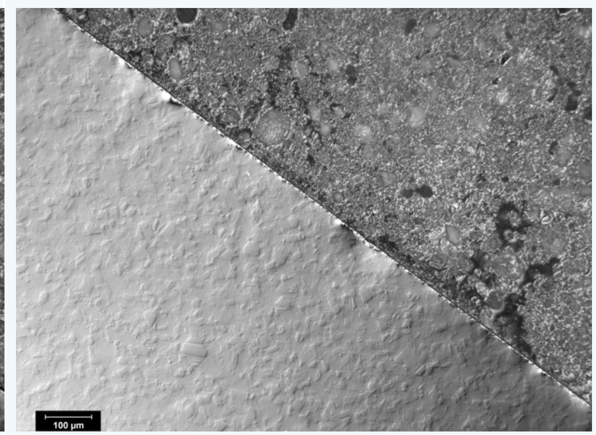
Metal Loss Results (240 hr)





- **Ni-base alloys: breakdown of a protective chromia scale**
  - An incubation period prior to rapid hot corrosion
  - Sometimes deep pit formation controls the behavior
  - Variability beyond, or at the edge of, the limited sample set of these tests to resolve

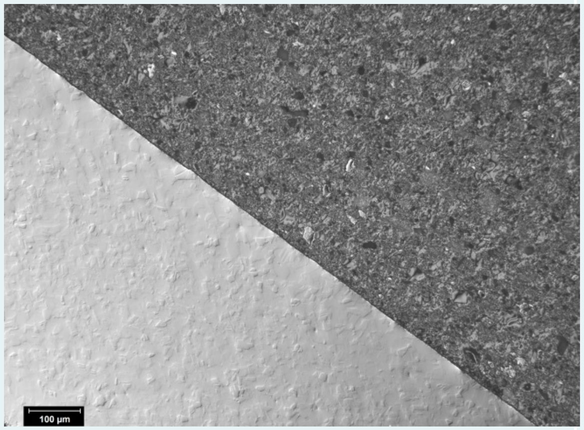
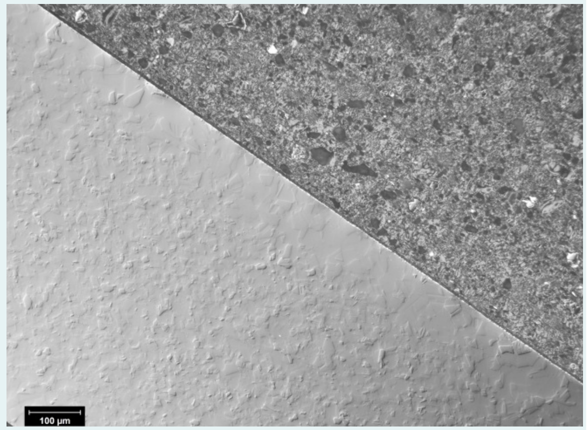
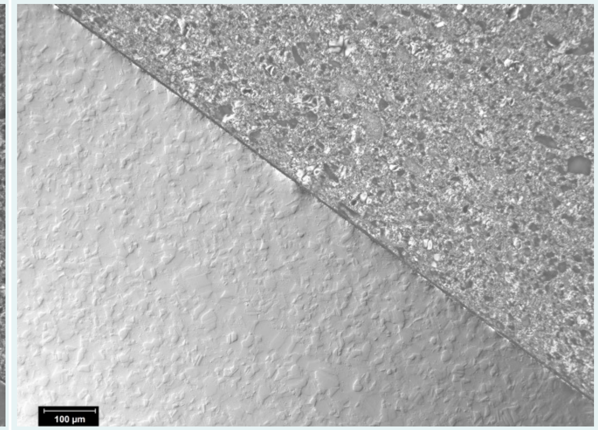
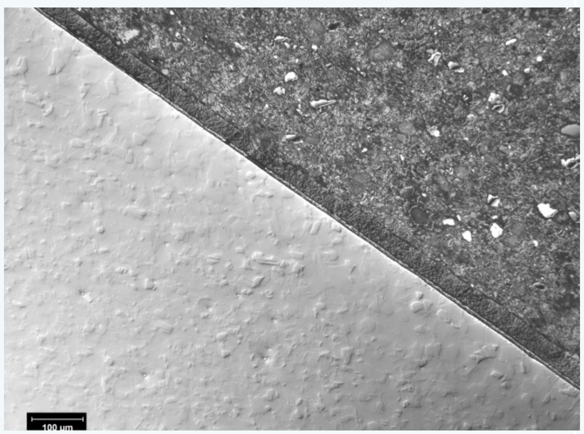
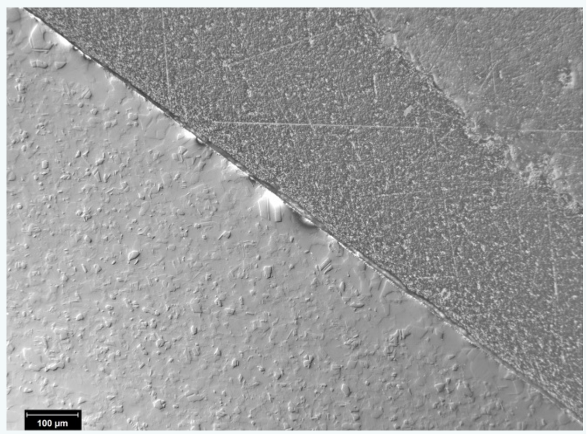
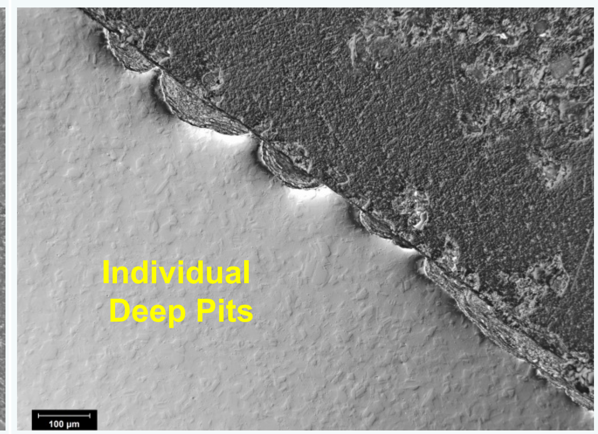
Effect of Mo 24 hr Exposure at 700°C with a 20% alkali iron trisulfate ash

	Ni 22Cr 0Mo	Ni 22Cr 1Mo	Ni 22Cr 8Mo
Air-Fired (0.3% SO_2)			
Oxy-Fired (0.9% SO_2)			

No effect from Mo or Gas Phase (SO_X, H_2O, CO_2) with a 20% alkali iron trisulfate ash

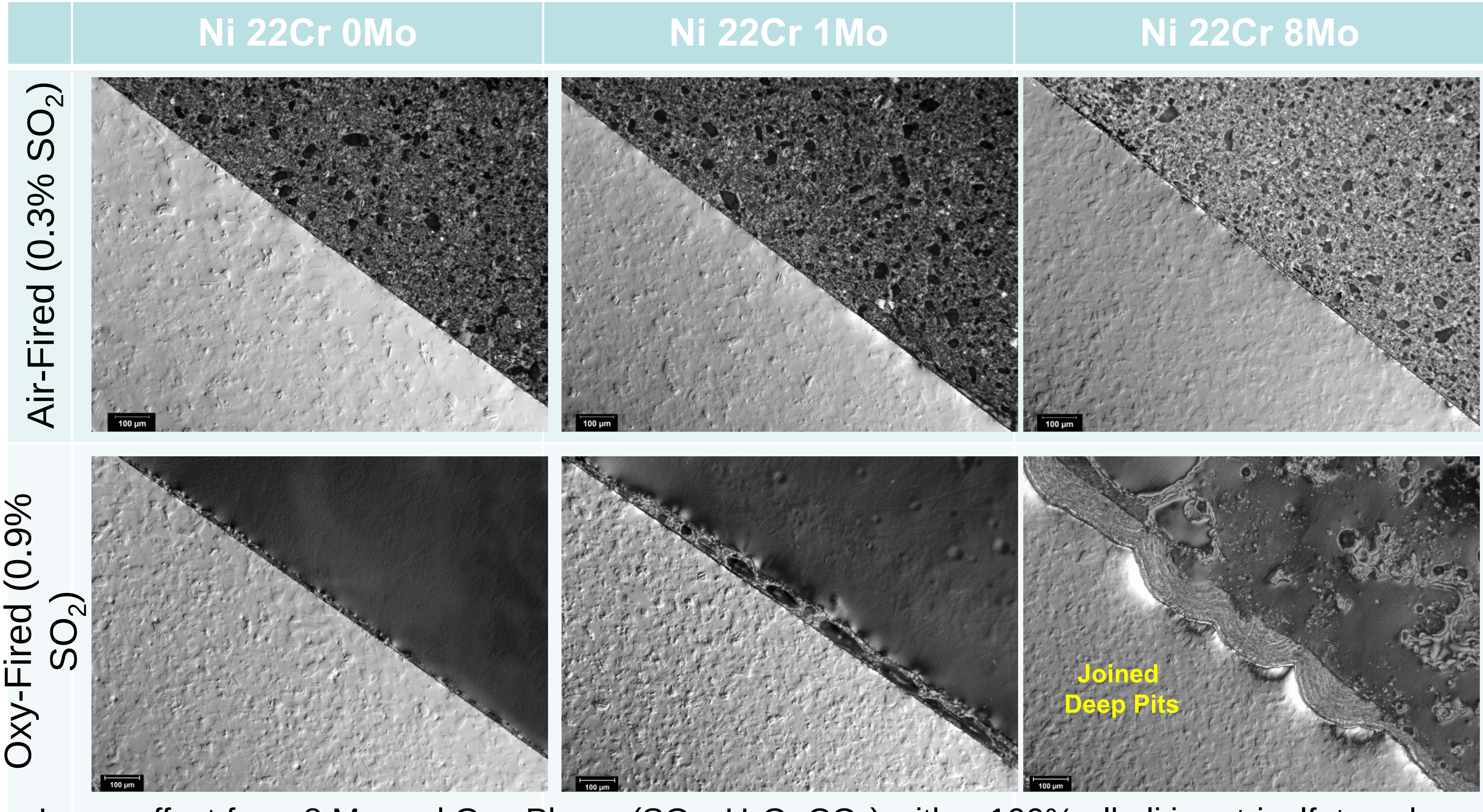
Effect of Mo

24 hr Exposure at 700°C with an 80% alkali iron

	Ni 22Cr 0Mo	Ni 22Cr 1Mo	Ni 22Cr 8Mo
Air-Fired (0.3% SO_2)			
Oxy-Fired (0.9% SO_2)			

Large effect from 8 Mo and Gas Phase (SO_X, H_2O, CO_2) with an 80% alkali iron trisulfate ash

Effect of Mo 24 hr Exposure at 700°C with a 100% alkali iron trisulfate ash

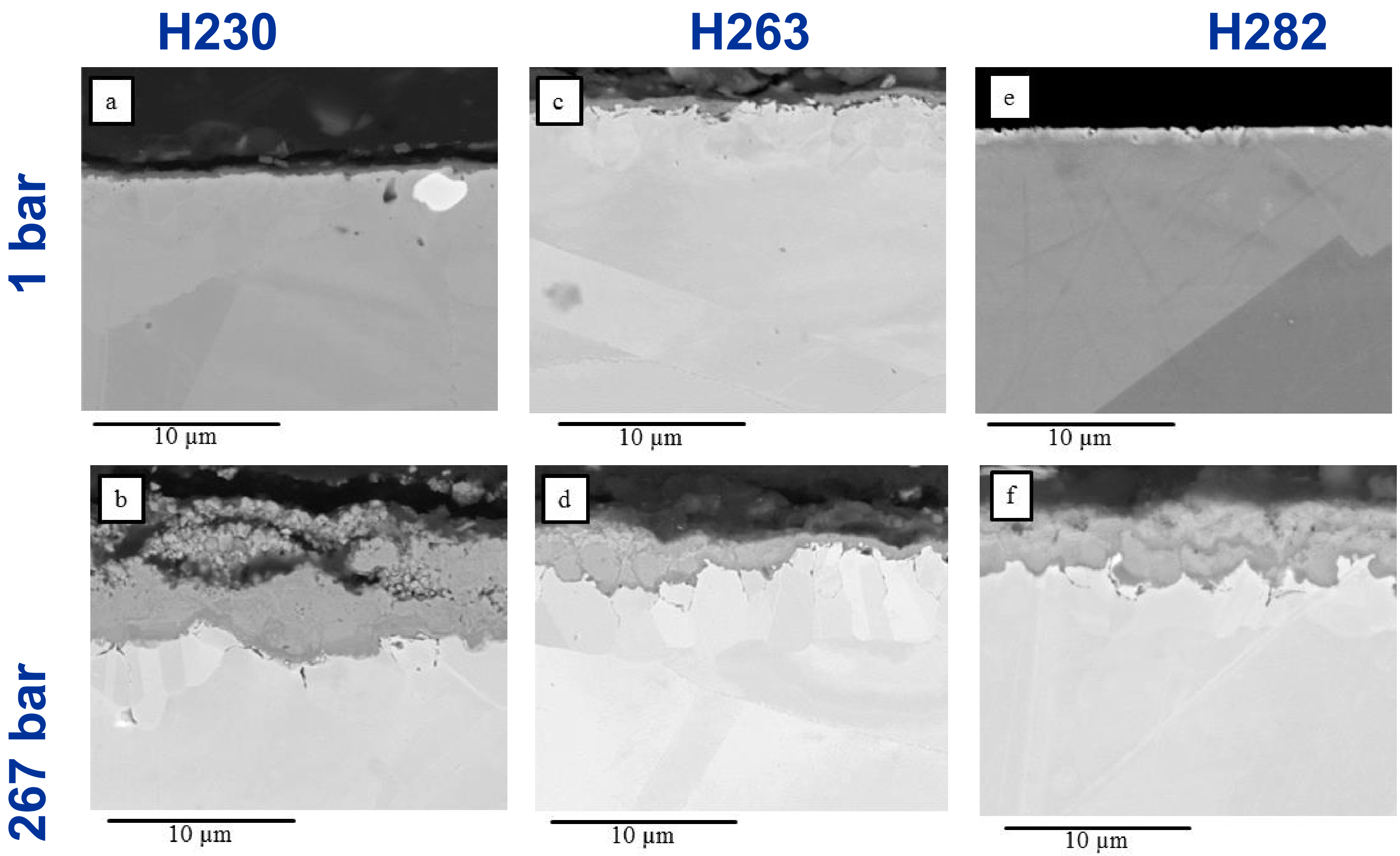


Large effect from 8 Mo and Gas Phase (SO_X, H_2O, CO_2) with a 100% alkali iron trisulfate ash
High levels of Mo decreases the incubation time for the transition to rapid corrosion

Steam Oxidation

- **Examine the effect of pressure on steam oxidation**
- **Advanced Ultra-supercritical (A-USC) steam applications**
- **Delays due to procurement of a replacement heater**
  - Tests restarted last week with a 500 hr exposure at 730°C and 207 bar (3000 psi)
- **Completed test at 670°C with 1 and 267 bar for about 300h**
  - 5 of 6 showed increased oxidation rates
  - Pure and compact chromia scales were not observed
  - Rates still within range for successful usage in A-USC boilers and turbines
  - IN625 needs additional tests and analyses
  - High pressure makes establishing and maintaining a chromia scale more difficult
  - Comparison with literature values shows a significant pressure effect somewhere above 105 bar

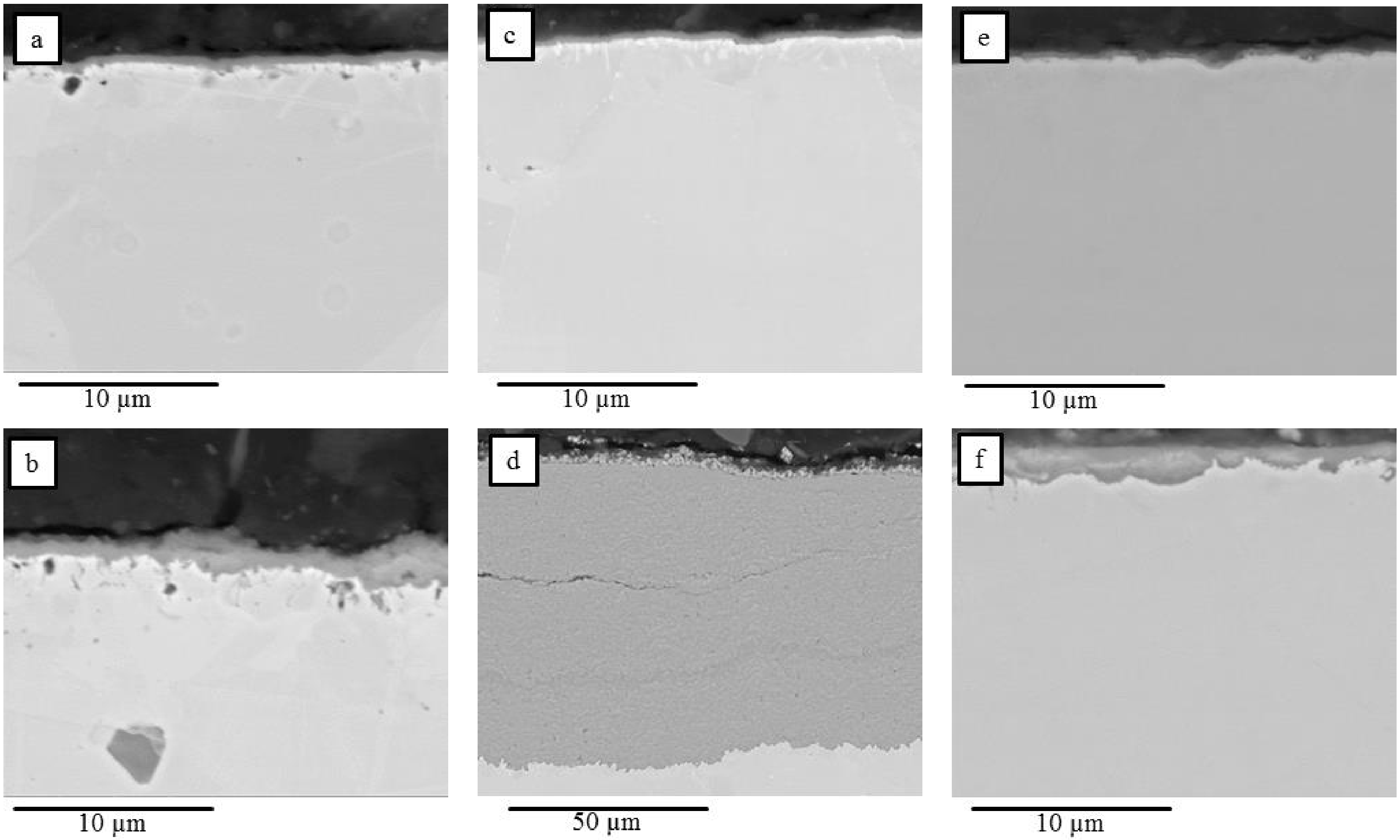
Ni-Base Alloy (670°C, 293 hr)



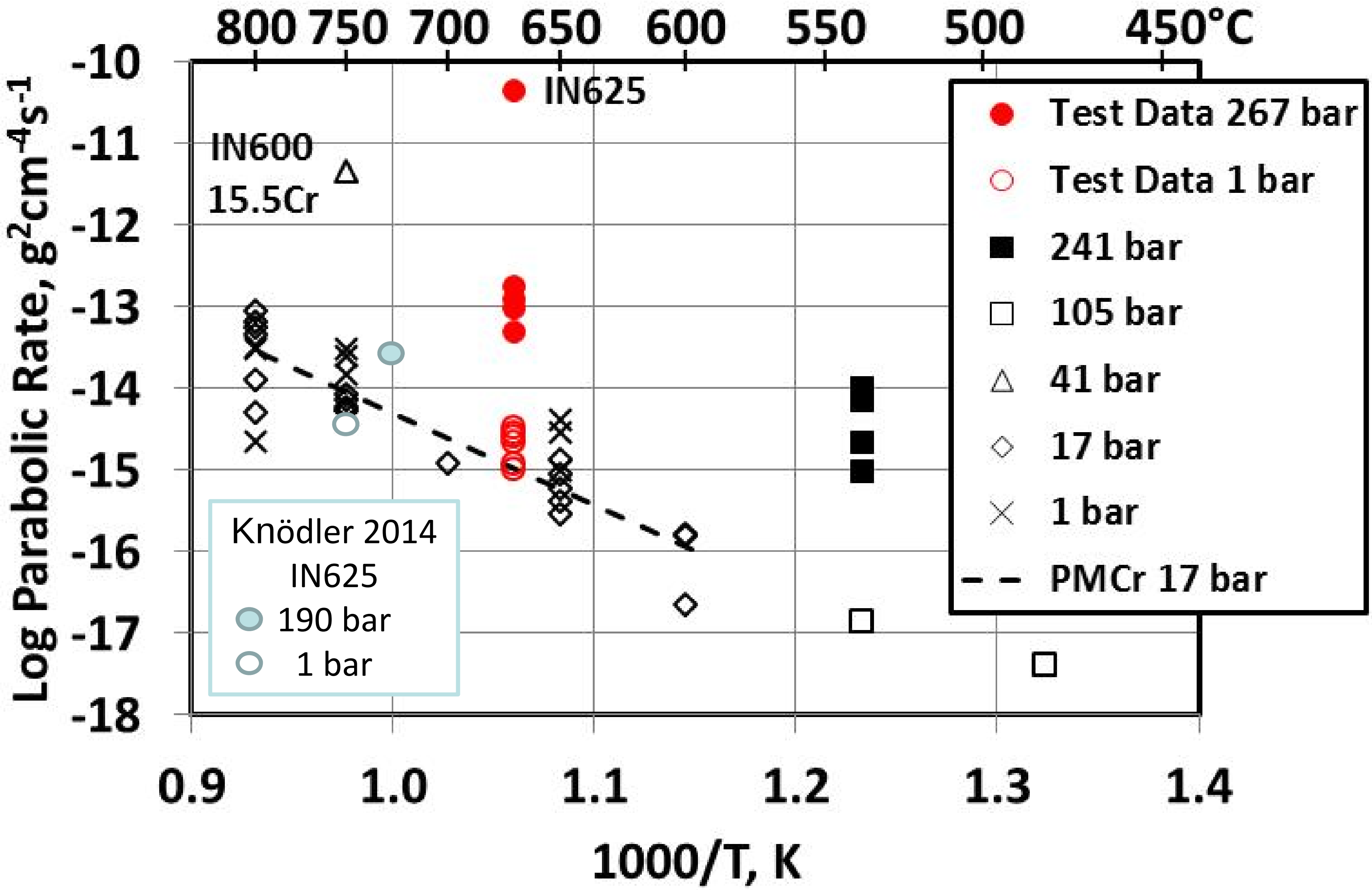
Ni-Base Alloy (670°C, 293 hr)

IN617 | IN625 | IN740

1 bar / 267 bar



Ni-base Test Data



Summary

Sulfur reduction:

- **Low sulfur remelt stock and alloys are achievable by reactive element addition in VIM or ESR techniques.**
- **Maintaining low S in the product ingot is achievable by good remelt practice.**

Fireside corrosion:

- **Coal ash corrosion results are highly variable—pitting makes clear conclusions hard (looking into comparing distributions)**
- **High levels (8) of Mo decrease the incubation time to rapid corrosion.**

Steam oxidation:

- **Seems to be a pressure effect above 105 bar**

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