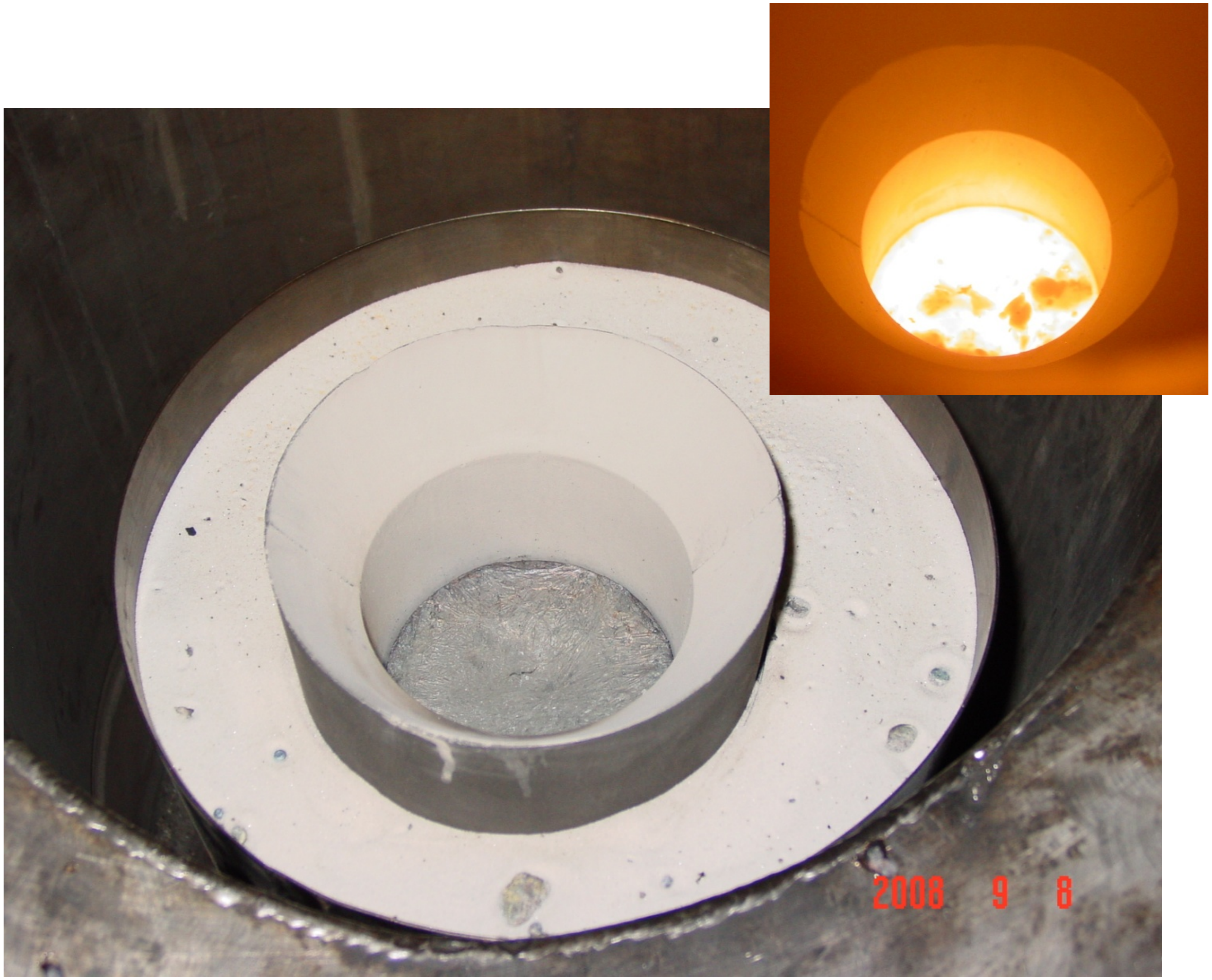
Addressing Materials Processing Issues for A-USC Steam Turbines

Paul D. Jablonski, and Jeffery Hawk

Challenges for A-USC Castings

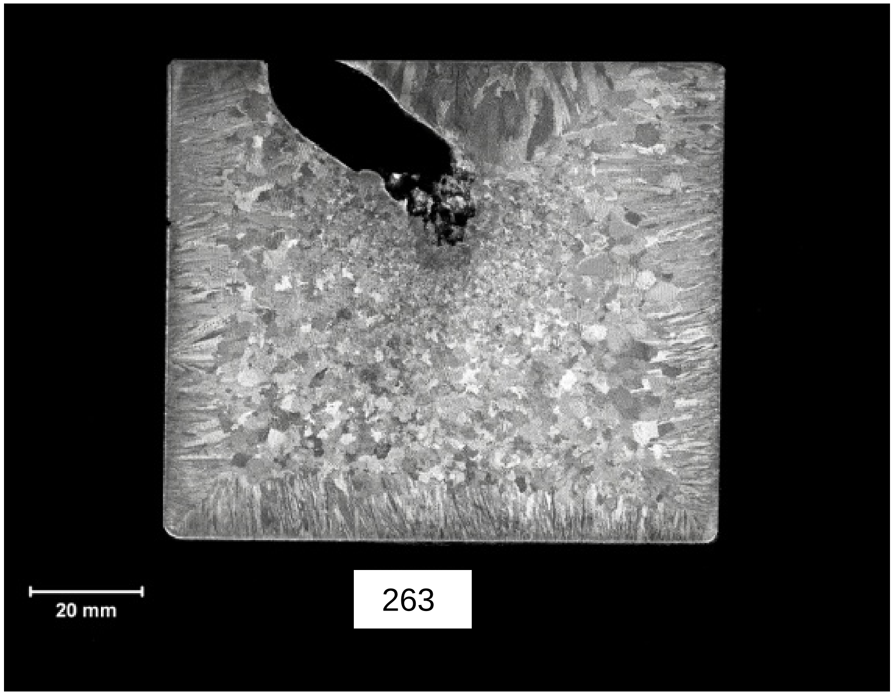
- **Conditions require Ni-based superalloys**
- **Alloys contain elements with high oxygen affinity such as Al and Ti**
- **Large pour weights (1-15T)**
- **Thick section components (100mm or more)**
  - Slow cooling rates
  - Segregation prone alloys
- **Our approach is to examine a suite of traditionally wrought Ni-based superalloys cast under conditions designed to emulate the full sized casting.**
- **Traditionally wrought alloys are being considered due to proven weldability in thick sections.**

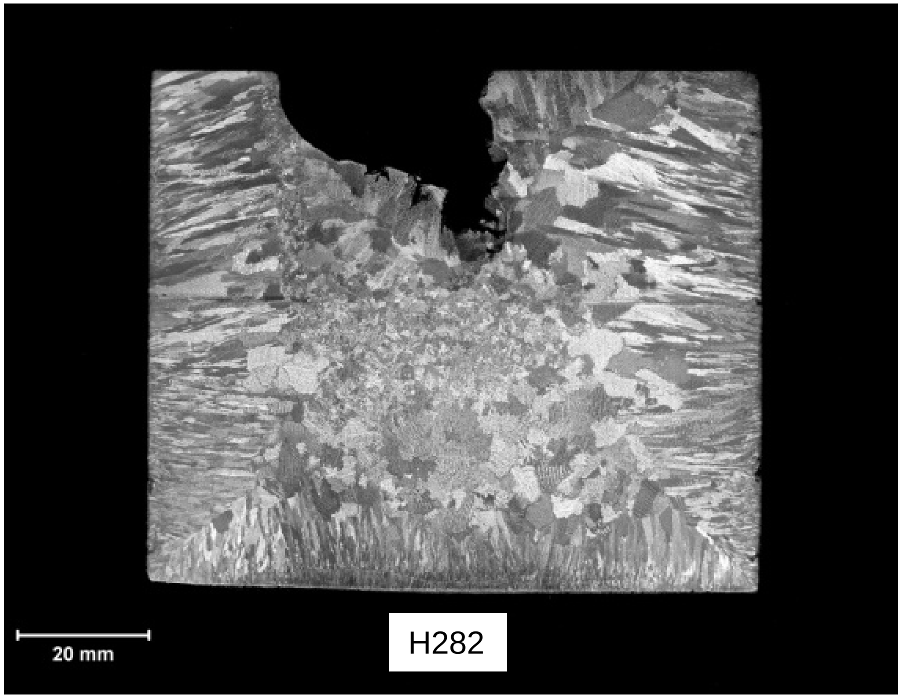
Casting Still in the Mold



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

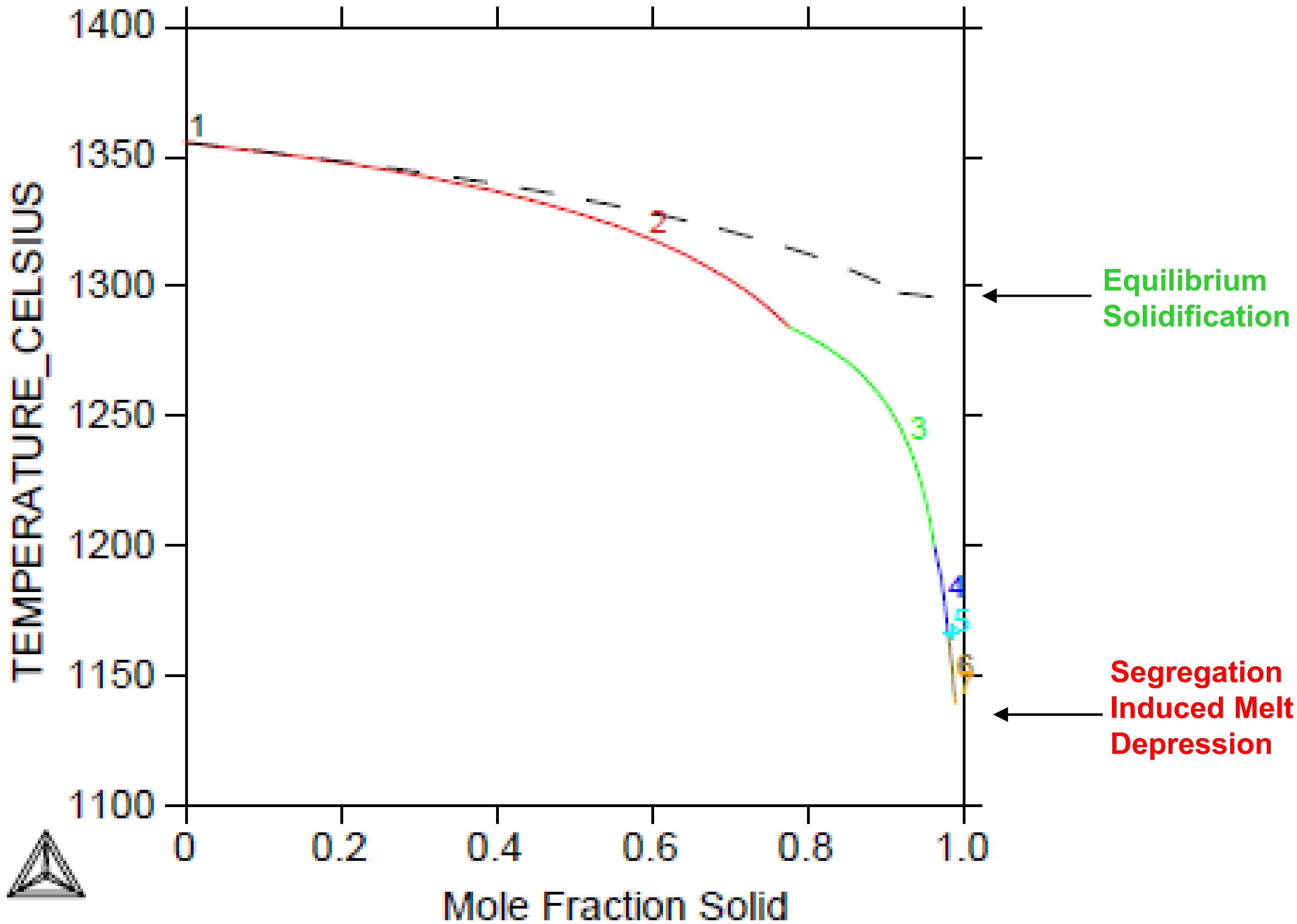




Ingots were sectioned to bisect the shrink cavity.

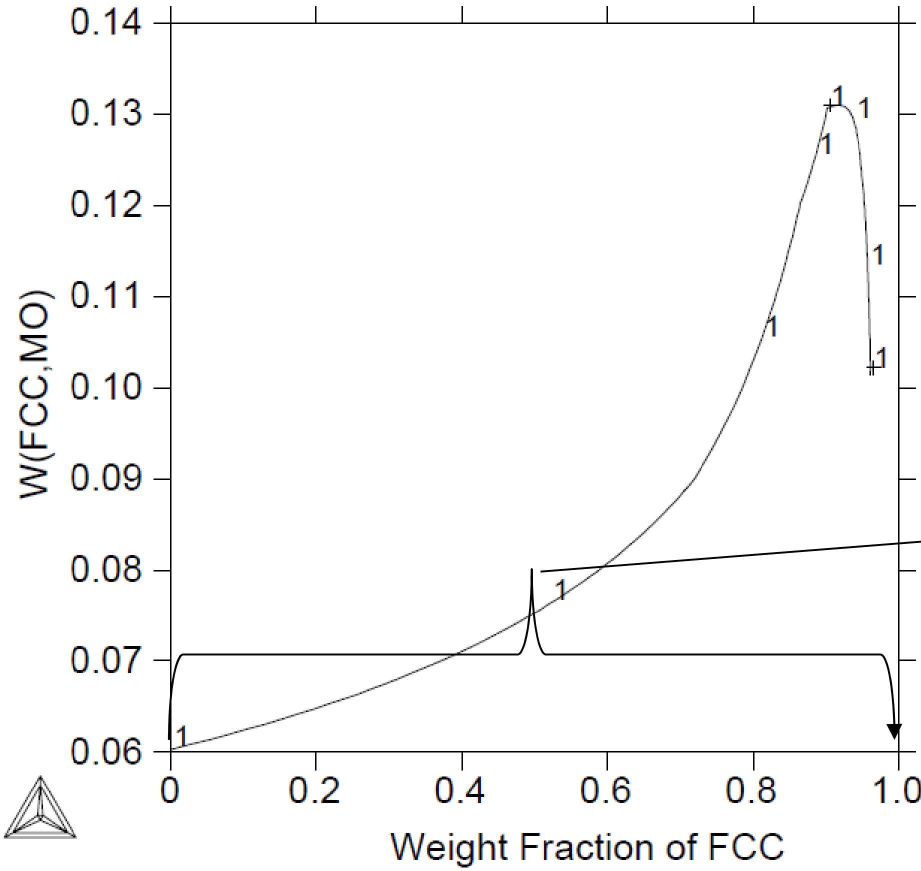
In general, the ingots have a columnar outer band ~1/4-1/3 of the radius thick and an equiaxed core. This is similar to the grain structure we would expect to observe in a large sand cast version of these alloys.

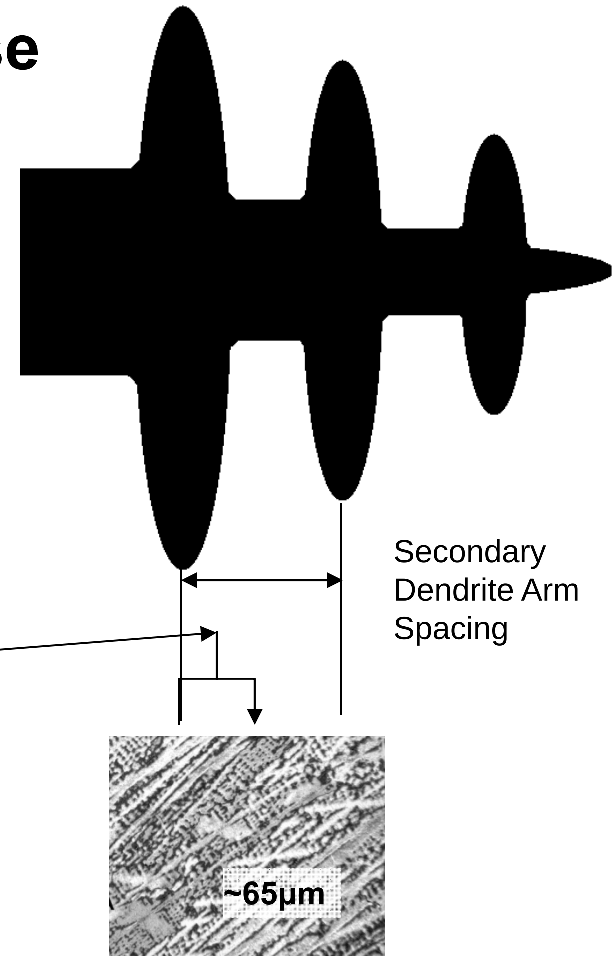
263—Solidification



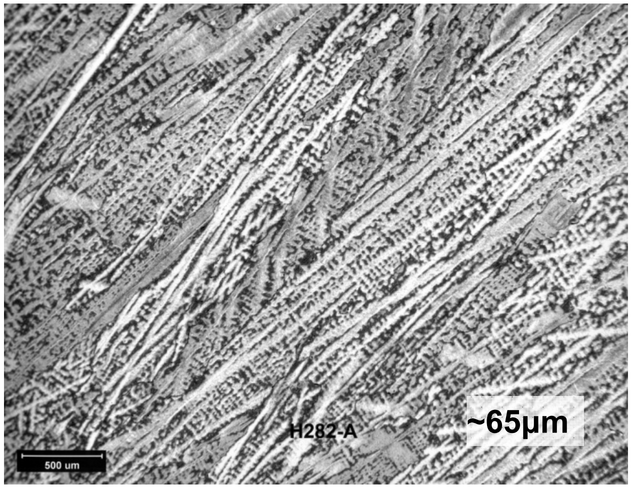
Variation of Mo in the FCC Phase

Segregation Within the FCC Phase

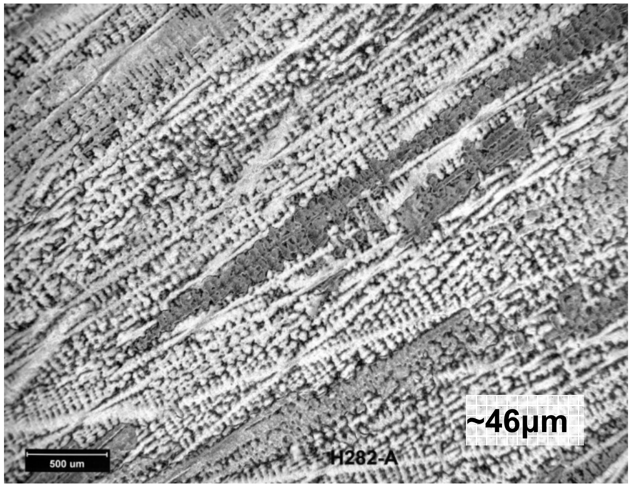


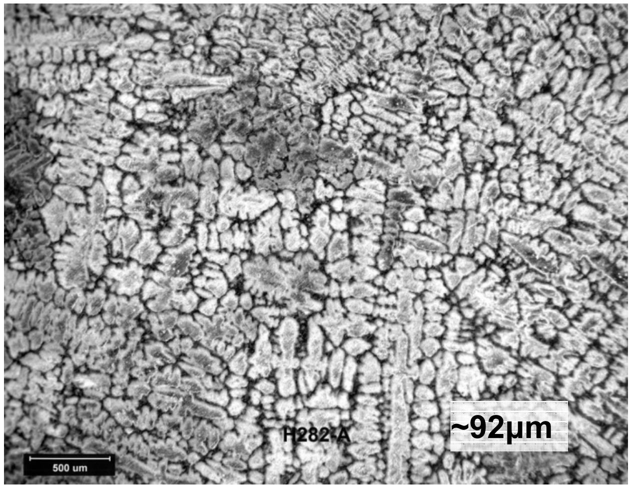


H282 Secondary Dendrite Arm Spacing

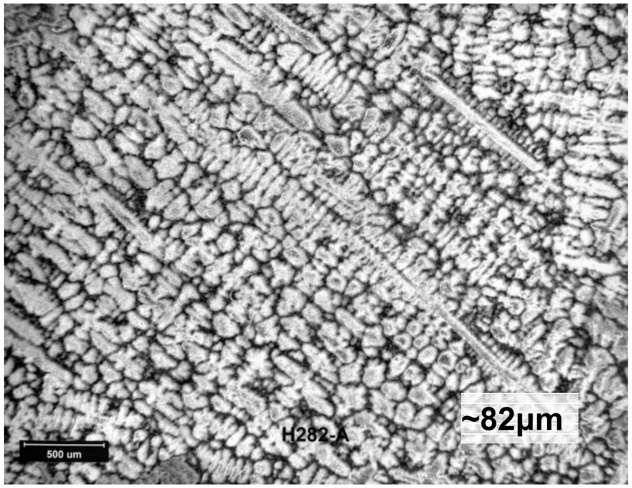


Columnar zone

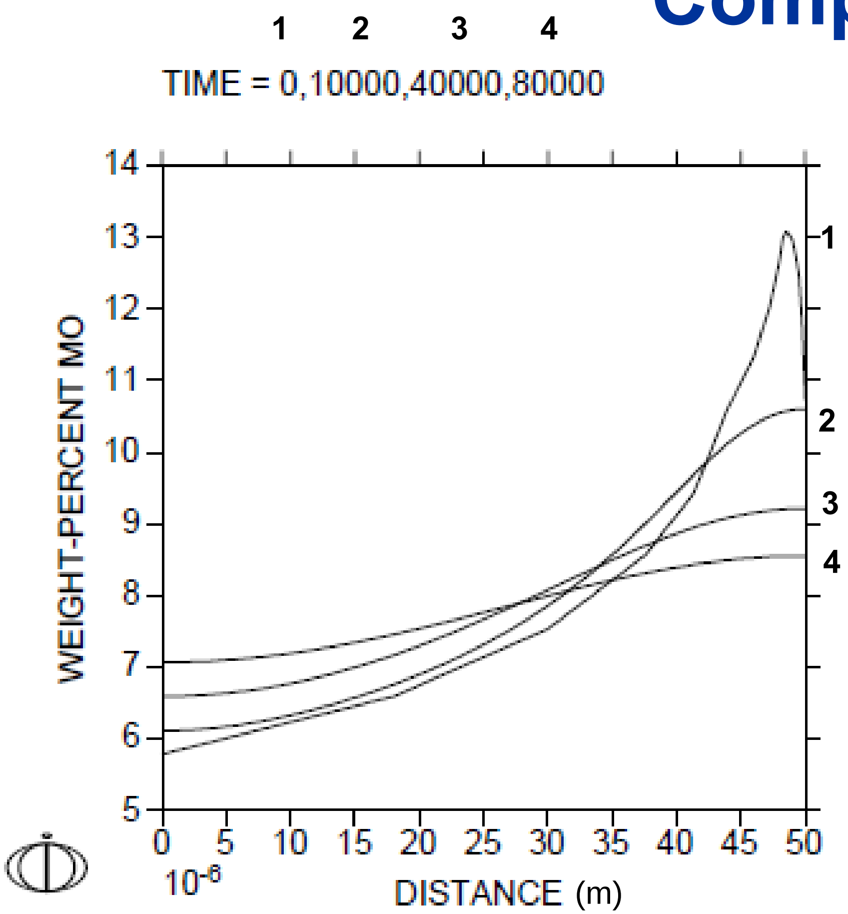




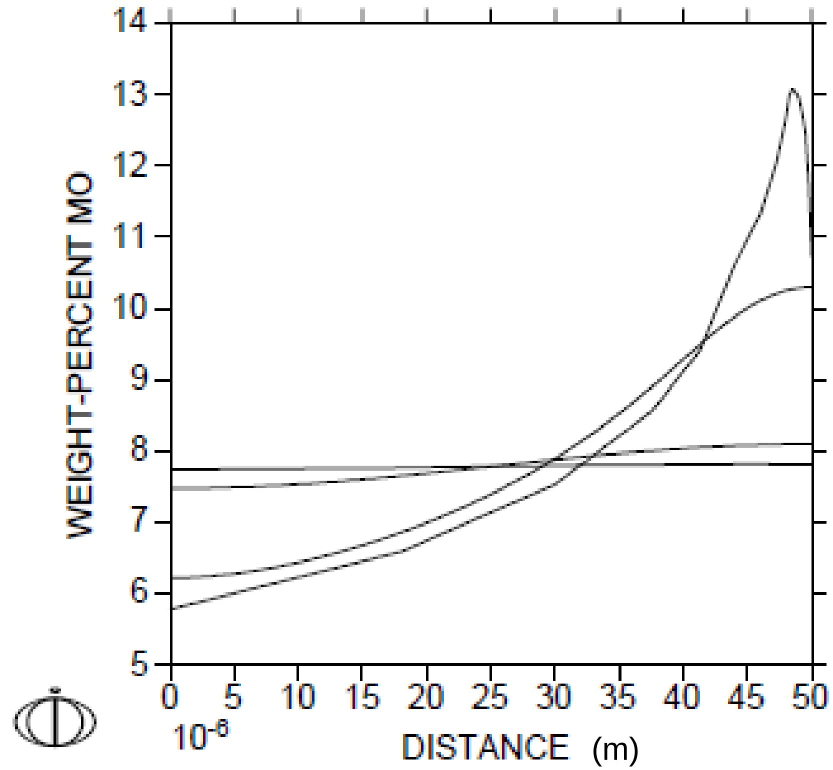
Equiaxed zone



H282—Homogenization Heat Treatment Comparison



Isothermal at 1100C



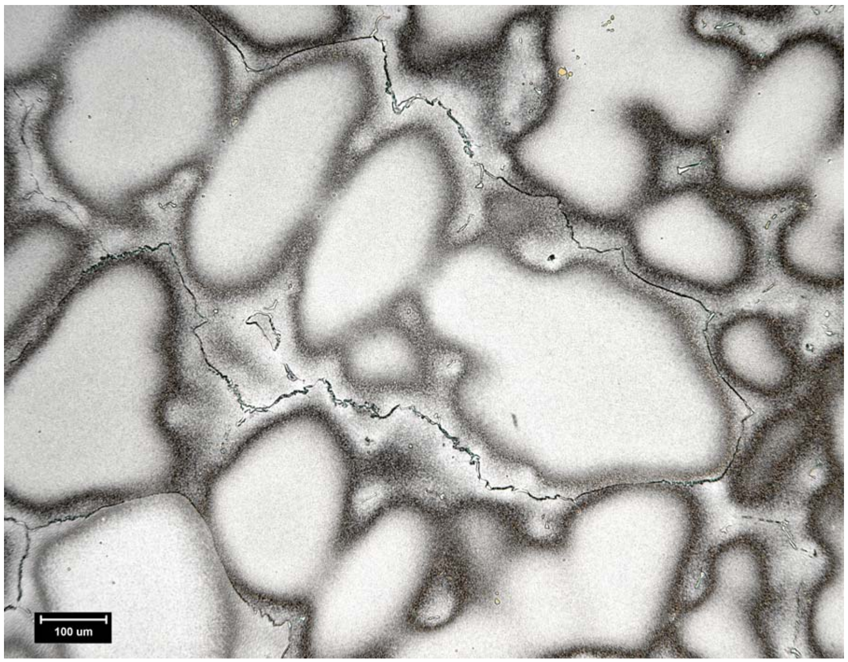
1100C/10,000s+1200C/remaining time

Patent Pending

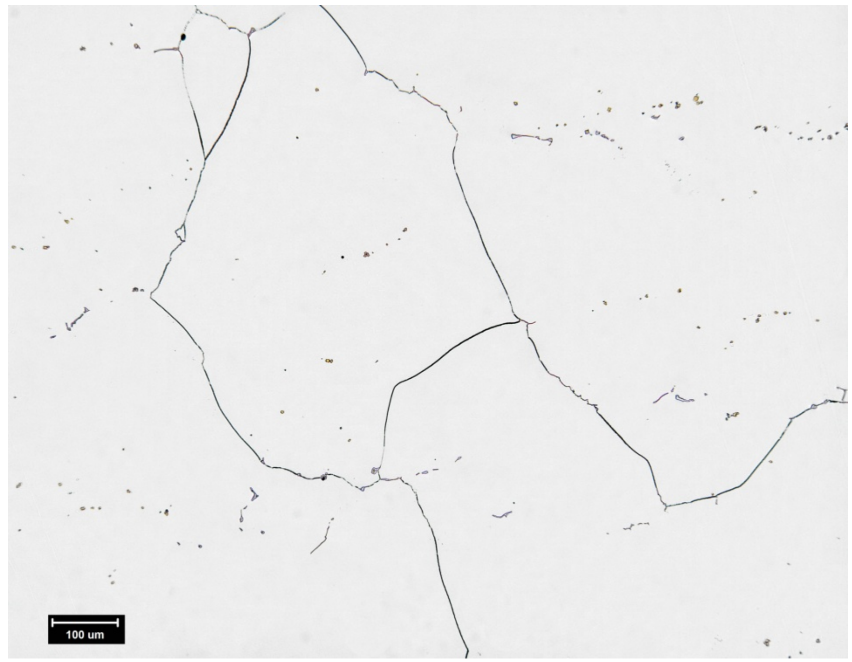
*Metall. Trans. B, **40B**, (2009) 182.*

As-Cast vs. Homogenized H282

Qualitative Confirmation of the Effectiveness of the Homogenization Heat Treatment

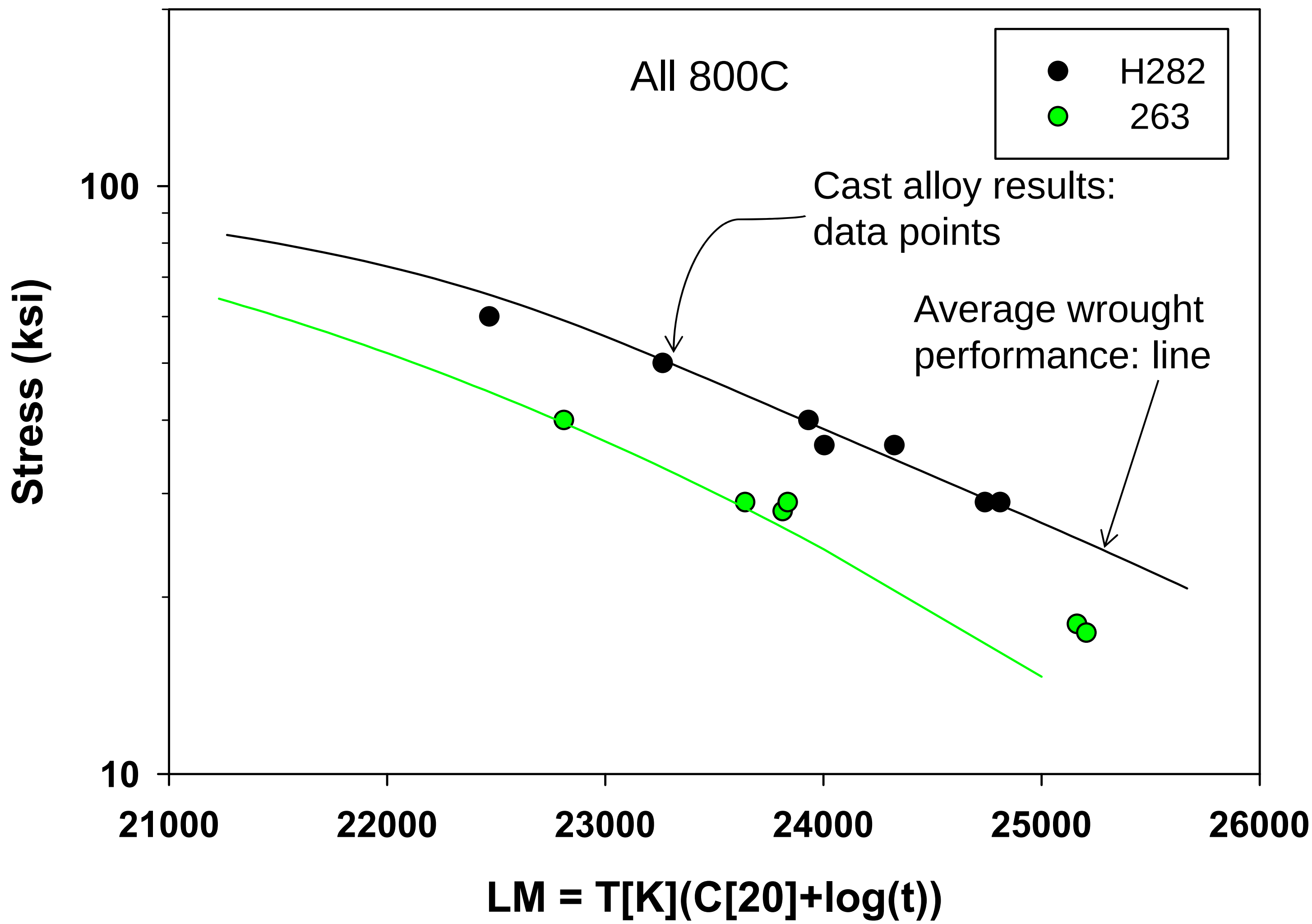


As-Cast



Homogenized

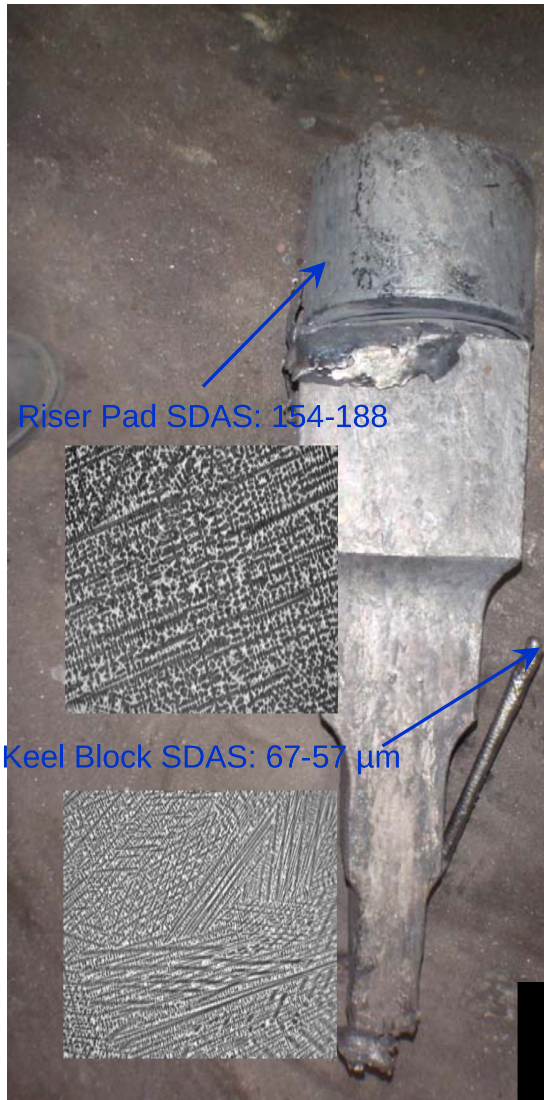
Comparison to Wrought Properties

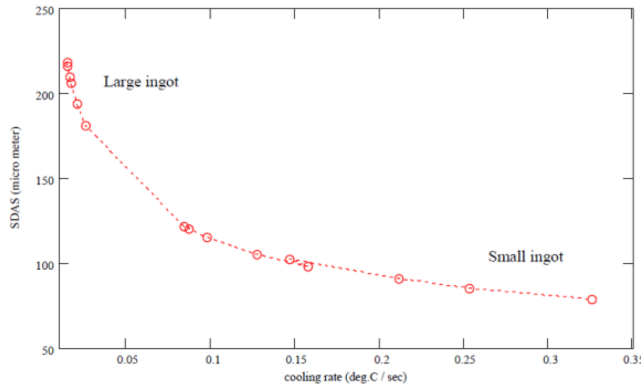


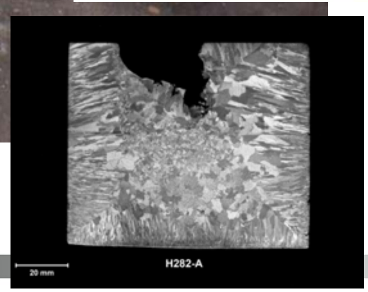
Section Summary: As-Cast Profiles

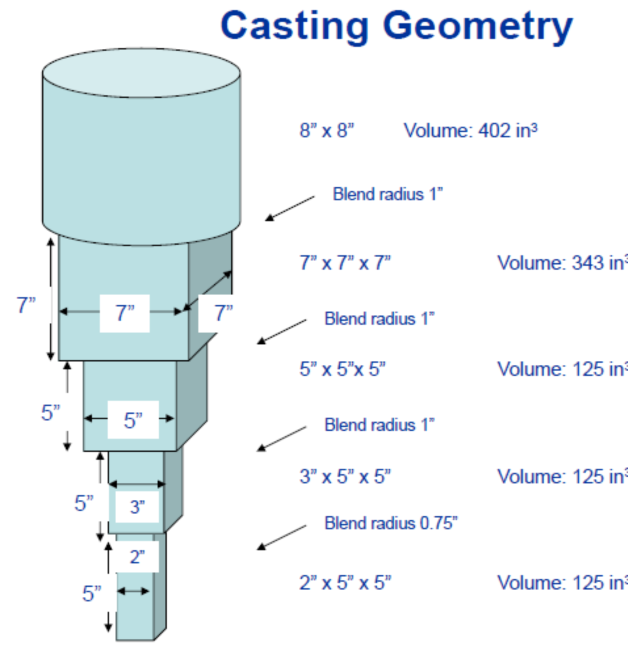
- **The refractory elements e.g., Mo, do not homogenize after ~22h/1100C**
- **Significant segregation of the second phase strengthening elements Al and Ti were observed to the point that 1/2-2/3 of the casting would be considered "lean"—larger impact on H282.**
- **Cr poor regions are predicted.**
- **Significant Co segregation was observed.**
- **Segregated regions in both alloys pose a problem with respect to non-equilibrium phases over long term exposure.**

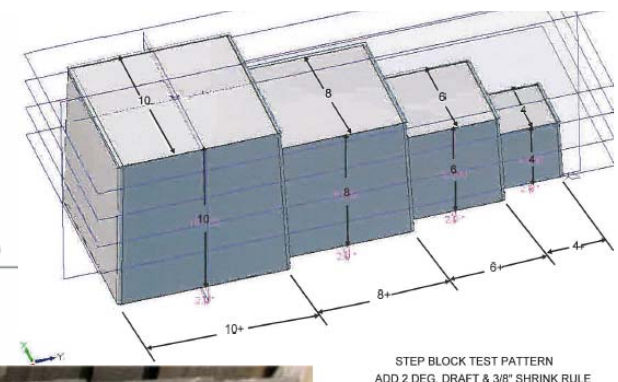
Trial Castings











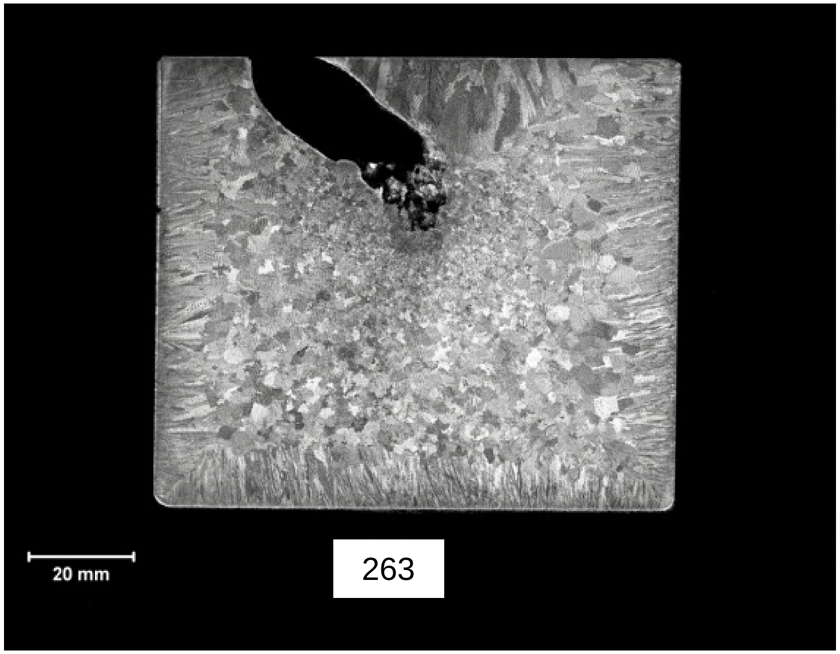
Interaction With Manufacturers H282

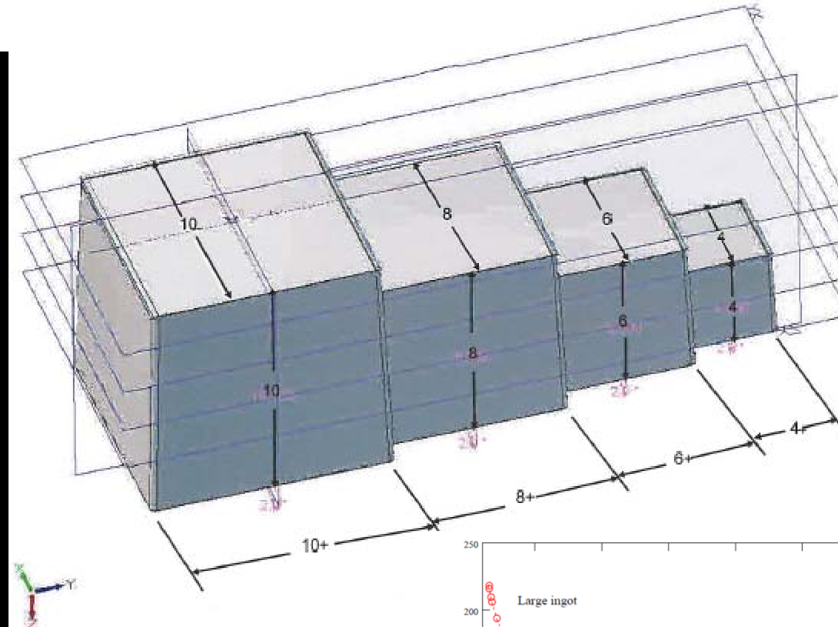
ESR Ingot

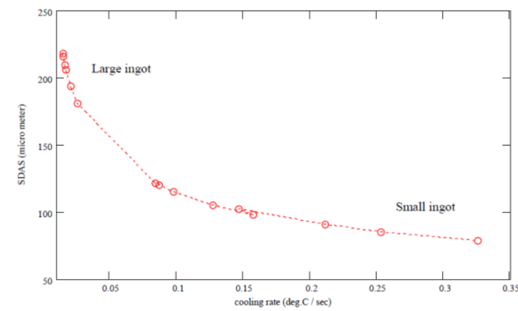
VAR Ingot: 24in Diameter x 71in long, ~10,000lb

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

Interaction With Manufacturers 263



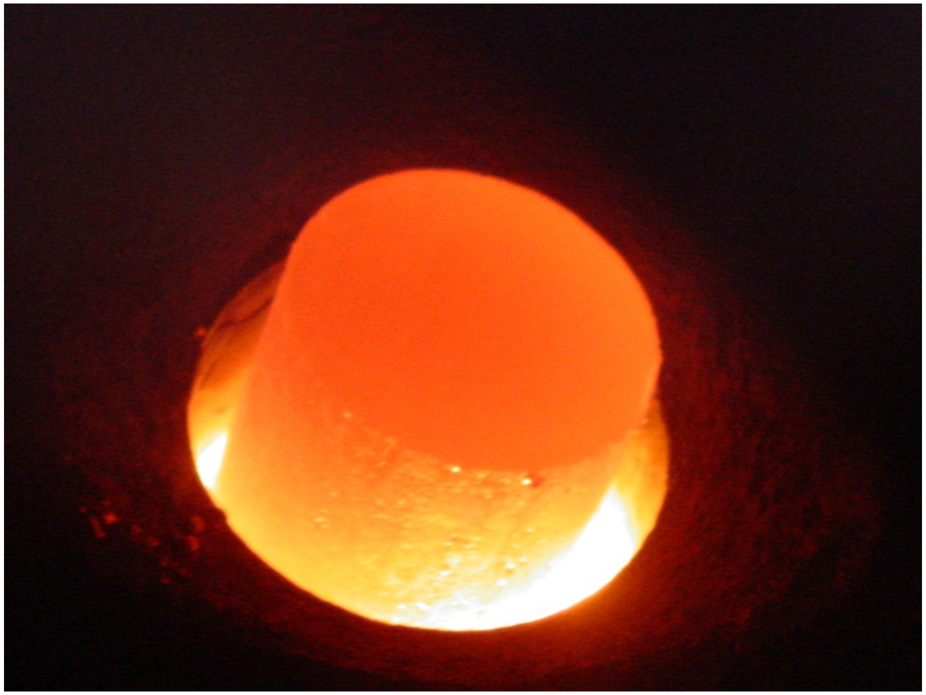




- Small ingots (15#): 1100C/3h + 1200C/9h
- Flowserve (1000#): 1100C/1h + 1200C/4h + 1250C/18h; Mo 91.4-108.5%
  - Current restrictions 1190C in-house, 1232C local vendor:
  - **1100C/1h + 1190C/44h;** Mo 91.6-108.3%
  - 1100C/1h + 1200C/4h + 1232C/22h; Mo 91.1-108.8%

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 cycle on H282 and alloy 263 have been performed. The effect is particularly evident on H282 in short term creep.



The Practical Application of Minor Element Control in Small Scale Melts

Paul D. Jablonski and Jeffrey A. Hawk

The Issue of Sulfur

- **Sulfur is detrimental in Ni-based superalloys**
  - Reduces oxide scale adhesion
  - Reduces grain boundary strength
  - Reduces weldability
- **Historical sulfur content of our alloys typically has been ~100ppm.**
- **$Nb_2(C,S)$ can be problematic.**
  - Low melting, embrittlement.
- **The majority of the sulfur comes from Cr additions.**
- **We are actively attempting to lower the sulfur to 10ppm or less.**

Reducing Sulfur by Vacuum Distillation

$$L = P\left(\frac{M}{RT}\right)^{0.5}$$

L = Langmuir loss rate [g/(cm^2.s)]

P = partial pressure of pure element at temperature [Pa = g/(cm.s^2)]

M = molecular weight of element [g/mole]

RT = gas constant times absolute temperature [erg/mole = g.cm^2/mole]

$$a = P_{sol}/P_{pure}$$

$$t = W/(LA)$$

Reducing Sulfur by Vacuum Distillation

$$t(T,C) = \frac{W}{A}\left(\frac{RT}{M}\right)^{0.5}\left(\frac{1}{aP}\right)$$

t = time to lose element from melt [s]; a function of T and C

T = absolute temperature [K]

C = weight fraction of element in melt

W = weight of element in the melt (taken as the melt weigh times the weight fraction) [g]

A = surface area of the melt (taken as the cross sectional area of the crucible) [cm^2]

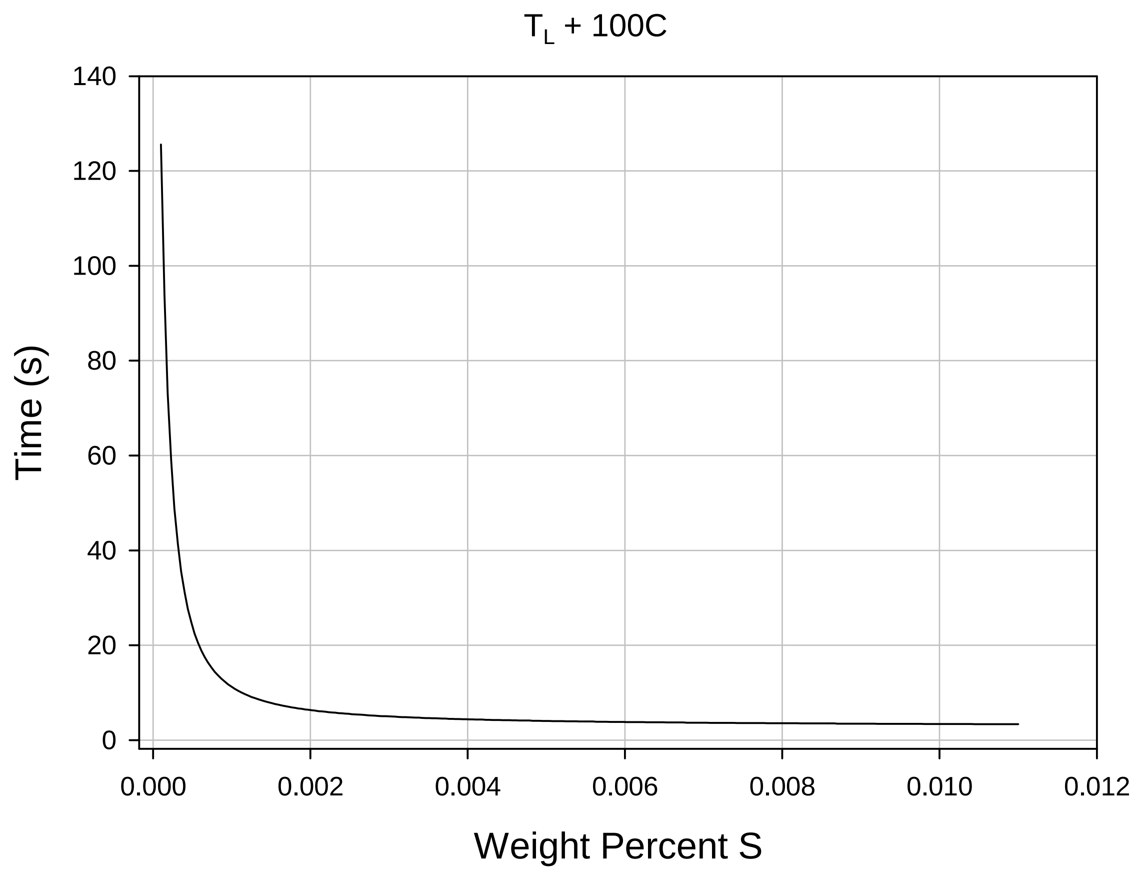
RT = gas constant times absolute temperature [erg/mole = g.cm^2/mole]

M = molecular weight of element [g/mole]

a = activity of element in the melt calculated with ThermoCalc (nominal alloy composition used)

P = partial pressure of pure element at temperature [Pa = g/(cm.s^2)]

Changing Composition



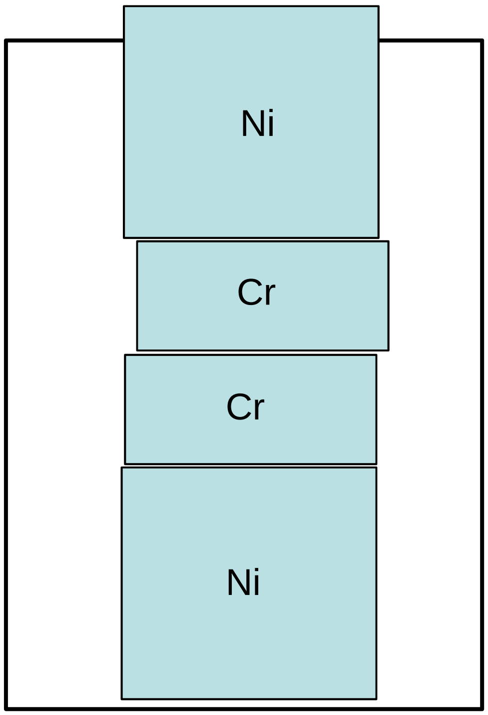
There is a tendency for the required time to increase as S content decreases. This is because the activity decreases.

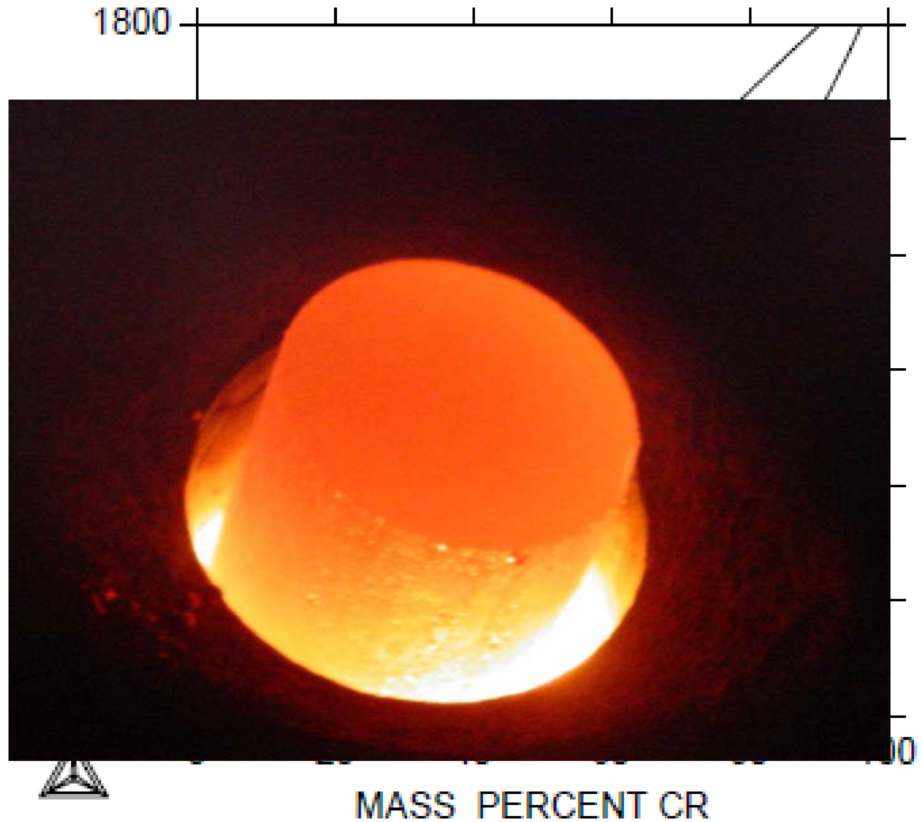
$$t(T,C) = \frac{W}{A}\left(\frac{RT}{M}\right)^{0.5}\left(\frac{1}{aP}\right)$$

Time and Temperature Vacuum Distillation Experiments

- **All with Ni-22Cr binaries**
- **Three hold times: 10m, 20m and 60m all at 100C superheat**
- **Three superheats: 50C, 100C and 150C all at 20m**
- **Resulting chemistry monitored.**

Melt Arrangement

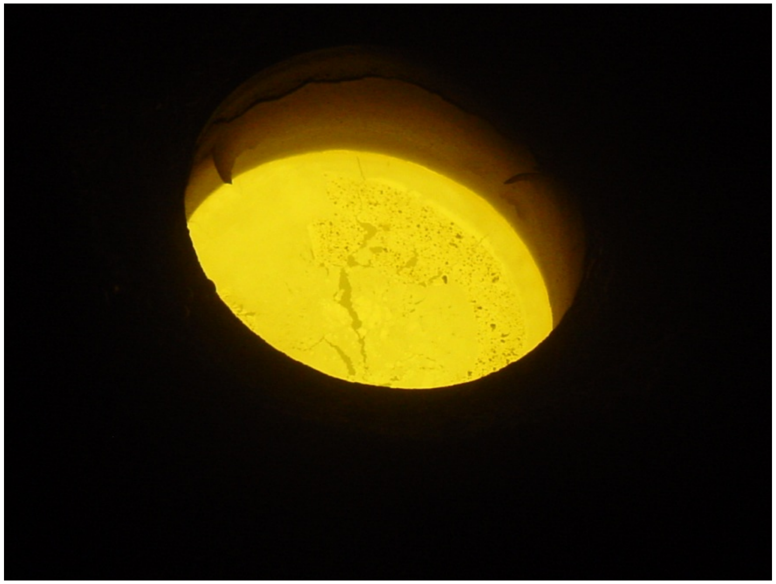




Ni: 1-2 ppm S
Cr: ~130 ppm S

Melt and Hold

Initial Melt



Melt and Hold

Resulting Chemistries From Superheat and Holding 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

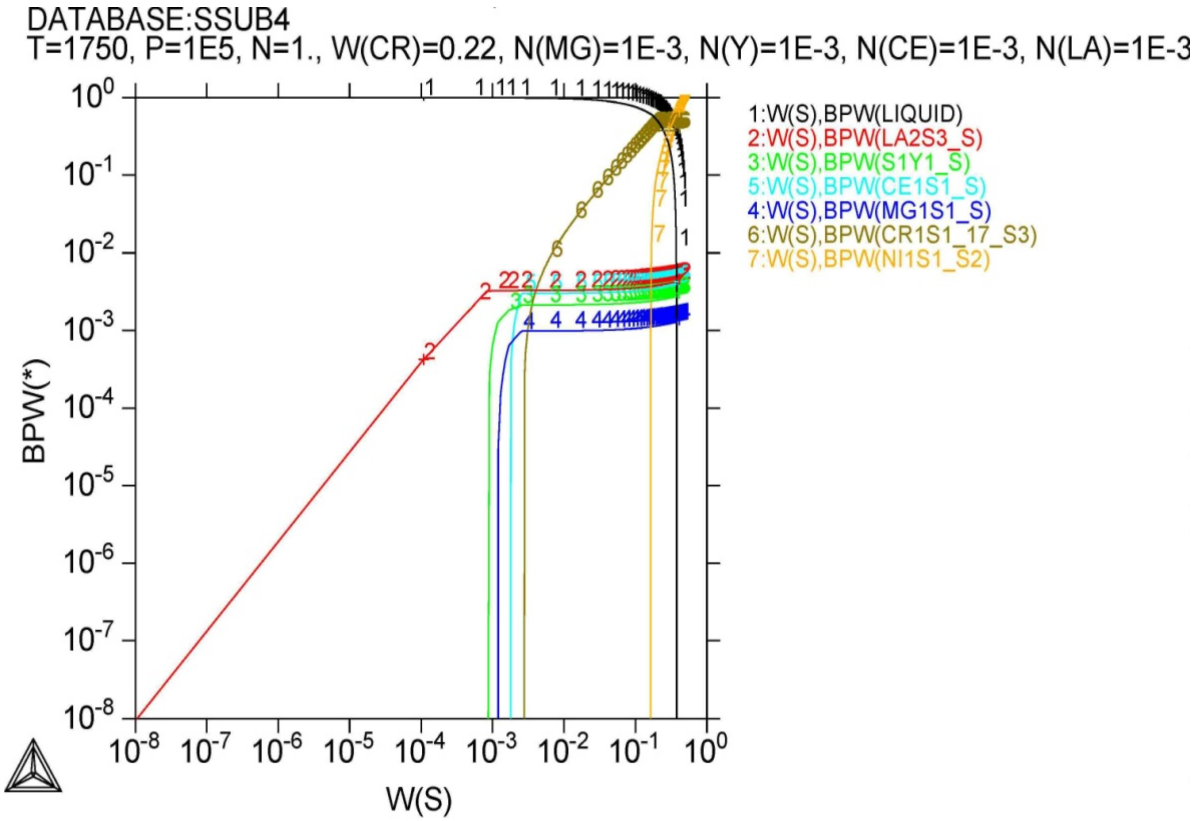
Reducing S in Ni alloys

We have completed several series of experiments and here are the highlights:

- It does not seem to be possible (yet) to reduce S by vacuum distillation. Hold times up to an hour and superheats up to 150C do not appear to be effective.
- We may need to revisit this however, since it was discovered that a mold wash previously used contains significant S. An alternative material has been identified and is currently being used.
- Additionally, vacuum levels and leak rates have been significantly improved. Ultimate vacuum typically on the order of 20-30 microns. More importantly, the leak rate is 0-0.1 microns/minute.
- Next is to evaluate the reduction of S with melt additions of reactive metals.

Trace Element Control by Reactive Element Addition

Let's consider a simple binary of Ni-22w/o Cr with 0.1 atomic percent of the elements from groups IIA and IIIA of the periodic table: Mg, Y, La, and Ce at 1477°C.



With Ca removed, the ranking in the relative amount of sulfides formed is:

La > Ce > Y > Mg

The critical S level ranking is as follows:

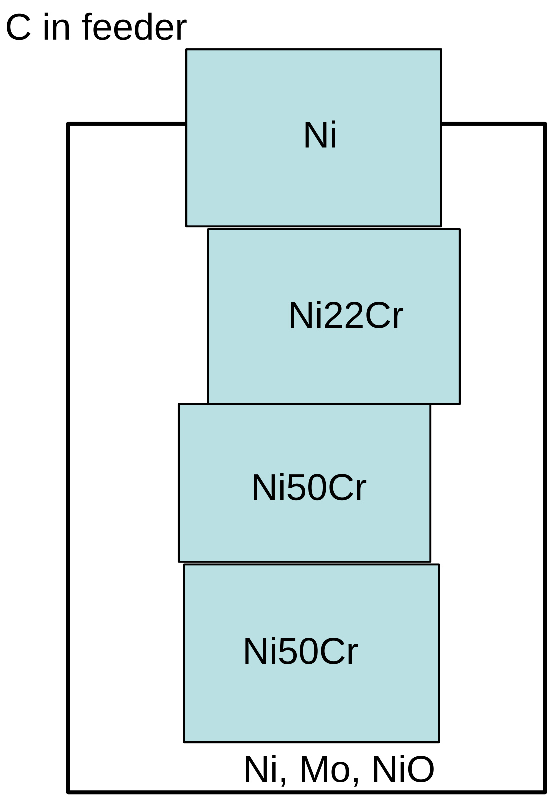
La > Ce > Y > Mg

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

Melt Arrangement for Ni-22Cr-xMo-0.05C



Estimate: 5 ppm S
Actual: 11 ppm S

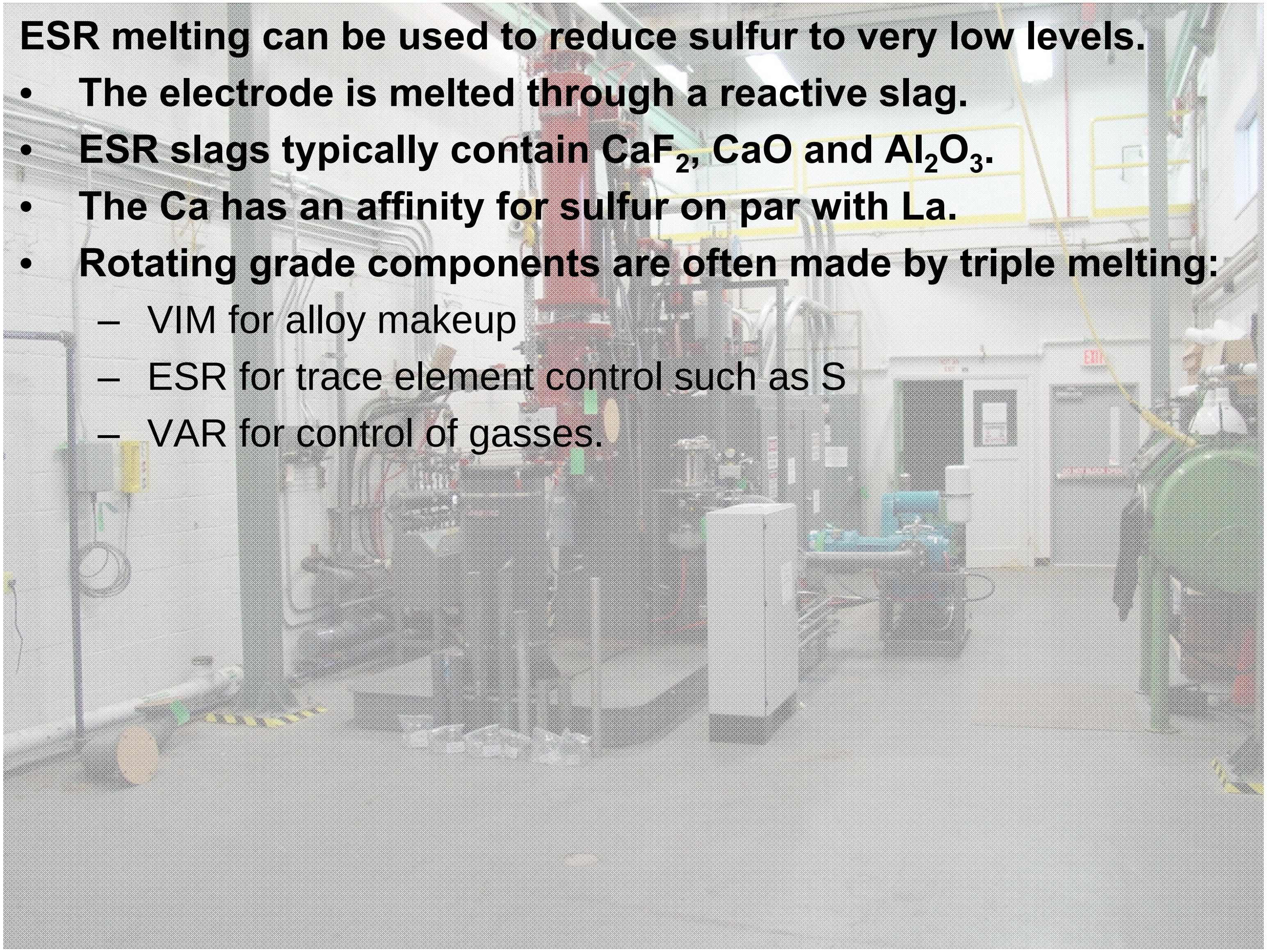
Model Reduced S Alloys

	Cr	Mo	C	N	O	S	La
Ni22Cr0Mo	22.18	0.016	0.04	49	8	11	21
Ni22Cr1Mo	22.04	0.99	0.05	54	14	4	3
Ni22Cr8Mo	22.04	7.77	0.05	64	11	11	3

Experimental alloys for corrosion studies.

N, O, S and La values are in PPM,
Rest are in w/o

Alternate Approach: ESR Melt Master Alloys



ESR melting can be used to reduce sulfur to very low levels.

- **The electrode is melted through a reactive slag.**
- **ESR slags typically contain CaF_2, CaO and Al_2O_3.**
- **The Ca has an affinity for sulfur on par with La.**
- **Rotating grade components are often made by triple melting:**
  - VIM for alloy makeup
  - ESR for trace element control such as S
  - VAR for control of gasses.

ESR Melts Up to 8in Diameter and ~400lb

Recent VAR and ESR Ingots

Summary

- Theoretically, sulfur can be reduced by vacuum distillation or gettering by elemental additions.
- Initial experiments have shown both to be effective, although gettering reduces S to the lowest level.
- Experimental heats have been made with low S melt stock.
- Our ongoing experiments are using ESR melting to reduce S.

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