NATIONAL ENERGY TECHNOLOGY LABORATORY

Addressing Materials Processing Issues for Steam Turbines: Cast Versions of Wrought Ni-Based Superalloys

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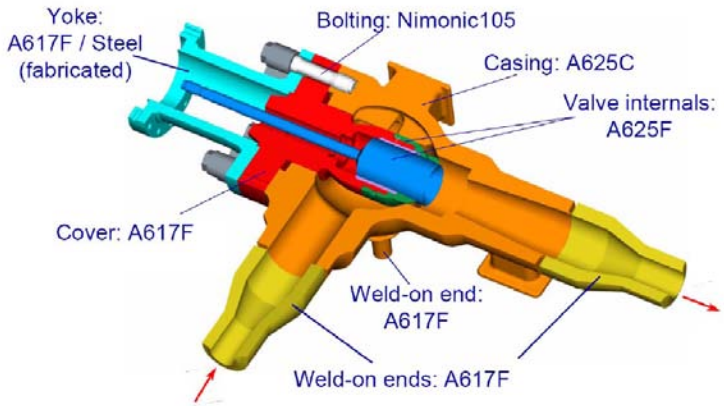
Technological Issues

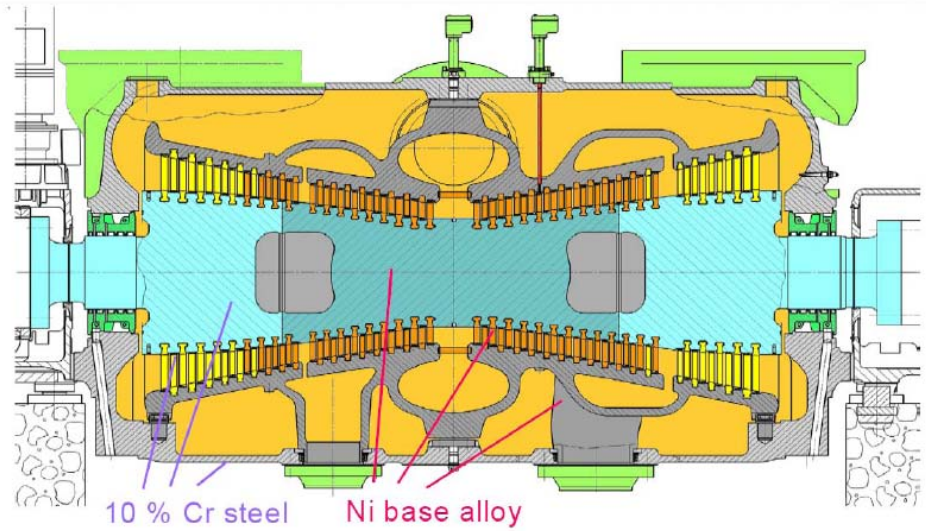
- **There is an immediate and continuing need for increased power production.**
- **Portfolio diversification dictates the use of coal.**
- **Increases in Temperature and Pressure increase efficiency and decrease CO_2 production along with other pollutants.**
- **Higher Temperature and Pressure place greater demands upon the Materials.**
- **Large castings are required for some components—many technical issues.**

Example Components

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



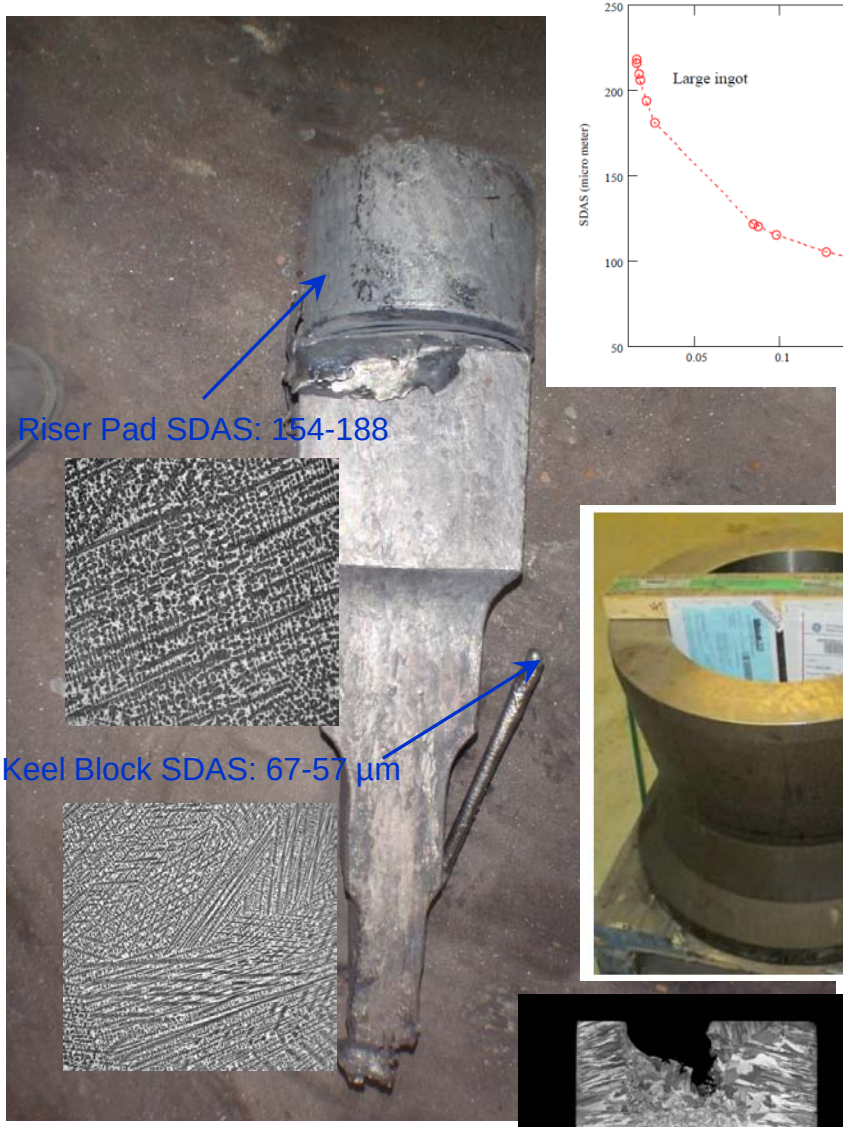
Valve Bodies

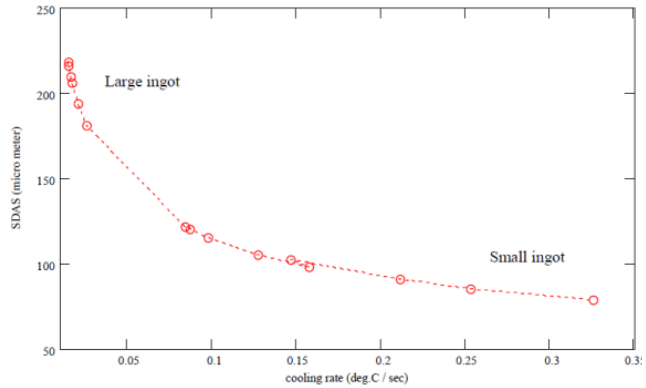


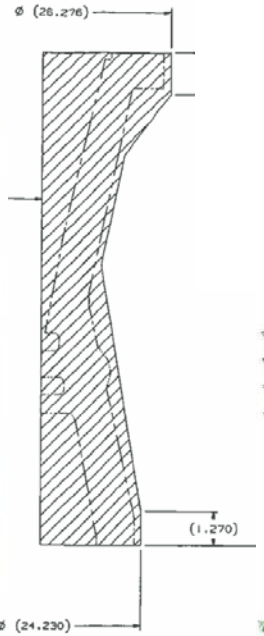
Turbine Casing

Courtesy Alstom

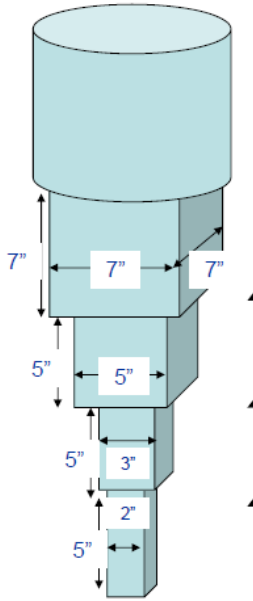
Trial Castings







Casting Geometry



8" x 8" Volume: 402 in³

Blend radius 1"

7" x 7" x 7" Volume: 343 in³

Blend radius 1"

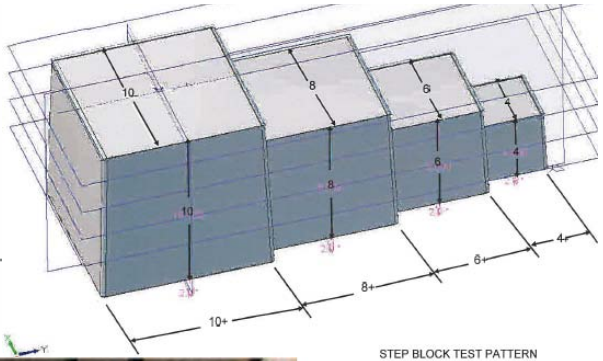
5" x 5"x 5" Volume: 125 in³

Blend radius 1"

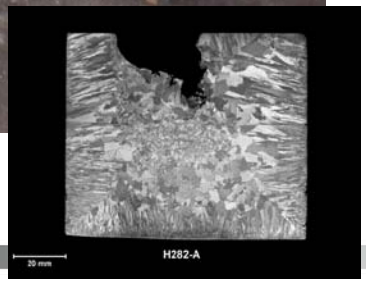
3" x 5" x 5" Volume: 125 in³

Blend radius 0.75"

2" x 5" x 5" Volume: 125 in³



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



LABORATORY

Interaction With Manufacturers-282

Homogenization Activities

ESR Ingot

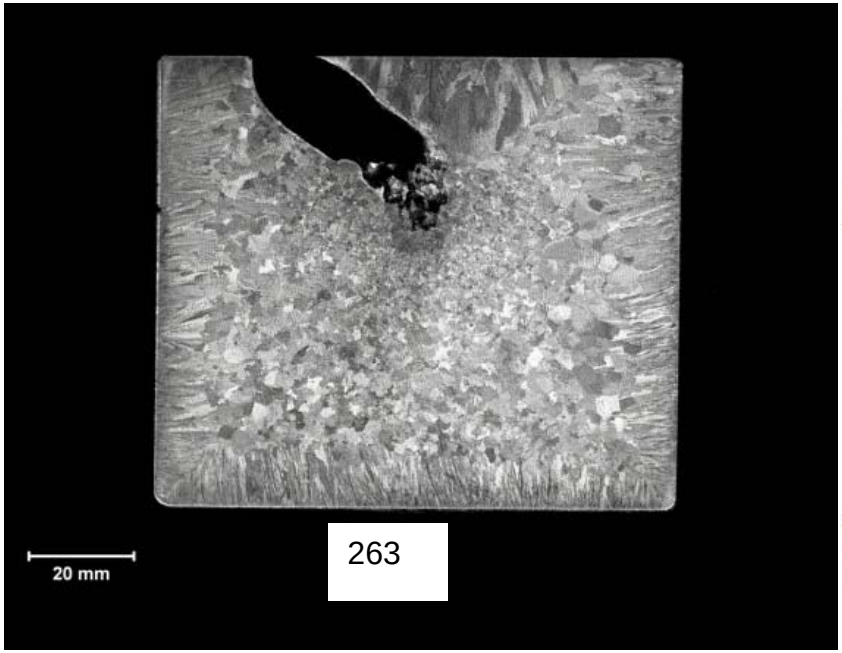
Casing

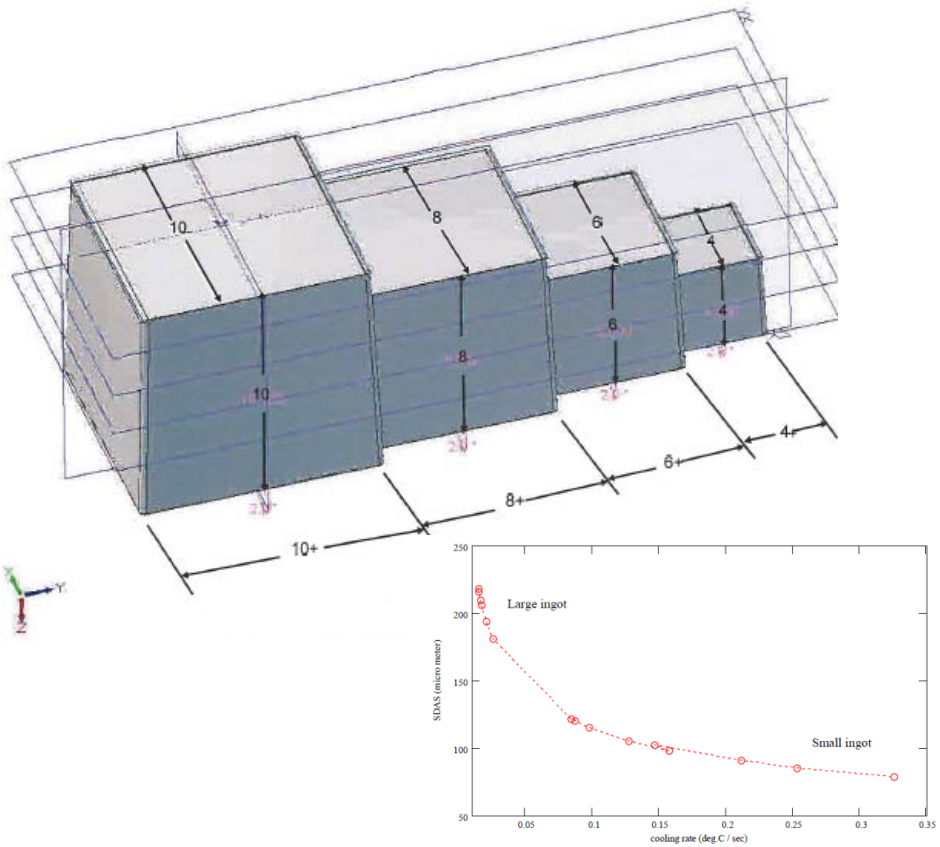
Special Metals ESR/VAR Ingot of Haynes 282

VAR Ingot: 24″ (dia.) x 71″ (length); ~10,000#

- NETL Small Ingots (15#): 1100°C/3h + 1200°C/9h
- Metaltek Step Block (300#): 1130°C/3h + 1200°C/3h + 1210°C/14h
- Flowserve Step Block (1000#): 1100°C/6h + 1200°C/48h
- SM ESR/VAR (10,000#): 1133°C/4h + 1190°C/8h + 1223°C/30h
- Metaltek Cylinder shape (1400#): 1125°C/1h + 1160°C/3h + 1190°C/6h + 1200°C/10h

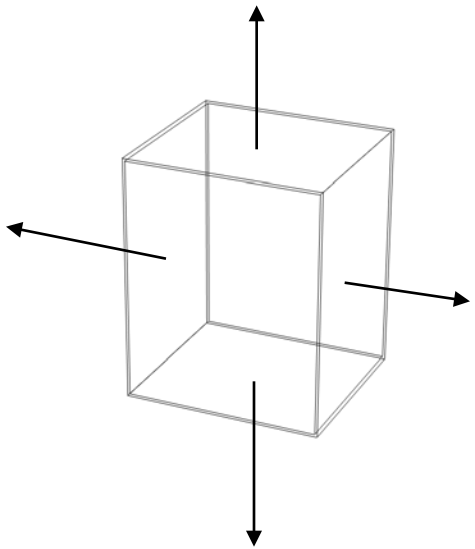
Interaction With Manufacturers 263

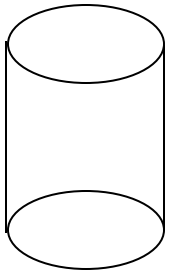




- Small ingots (15#): 1100C/3h + 1200C/9h
- Flowserve (1000#): 1100C/1h + 1200C/4h + 1250C/18h; Mo 91.4-108.5%
  - Current restrictions 1190C in-house, 1232C local vendor:
  - **1100C/1h + 1190C/44h;** Mo 91.6-108.3%
  - 1100C/1h + 1200C/4h + 1232C/22h; Mo 91.1-108.8%

Our Model Casting Geometry

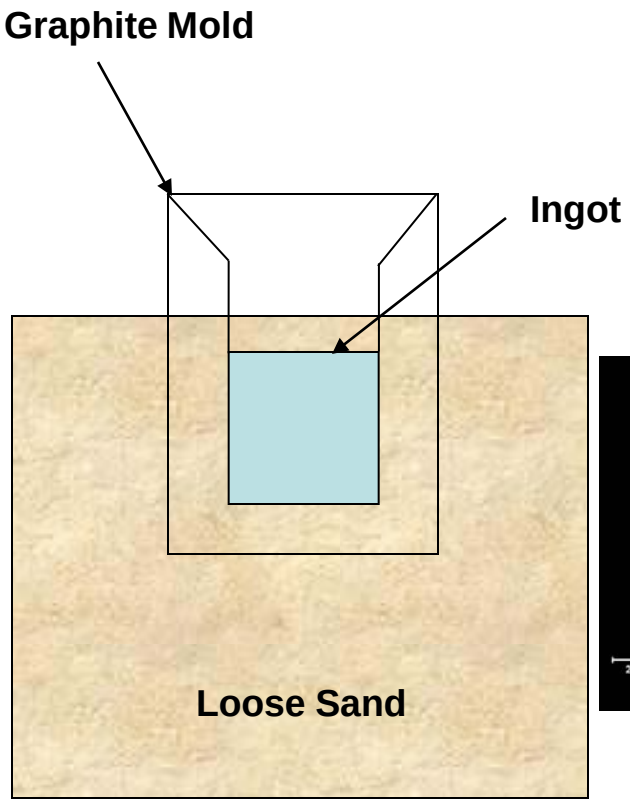


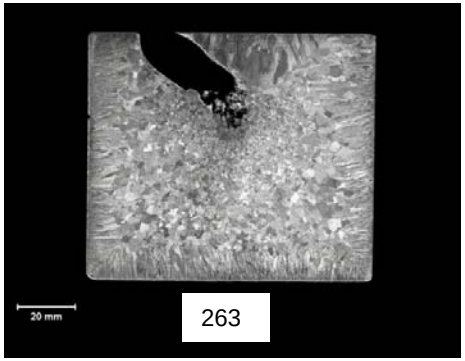


The actual component is nominally 4in thick and "infinite" in the other directions.

Our casting is nominally 4in in diameter and 4-5in tall.

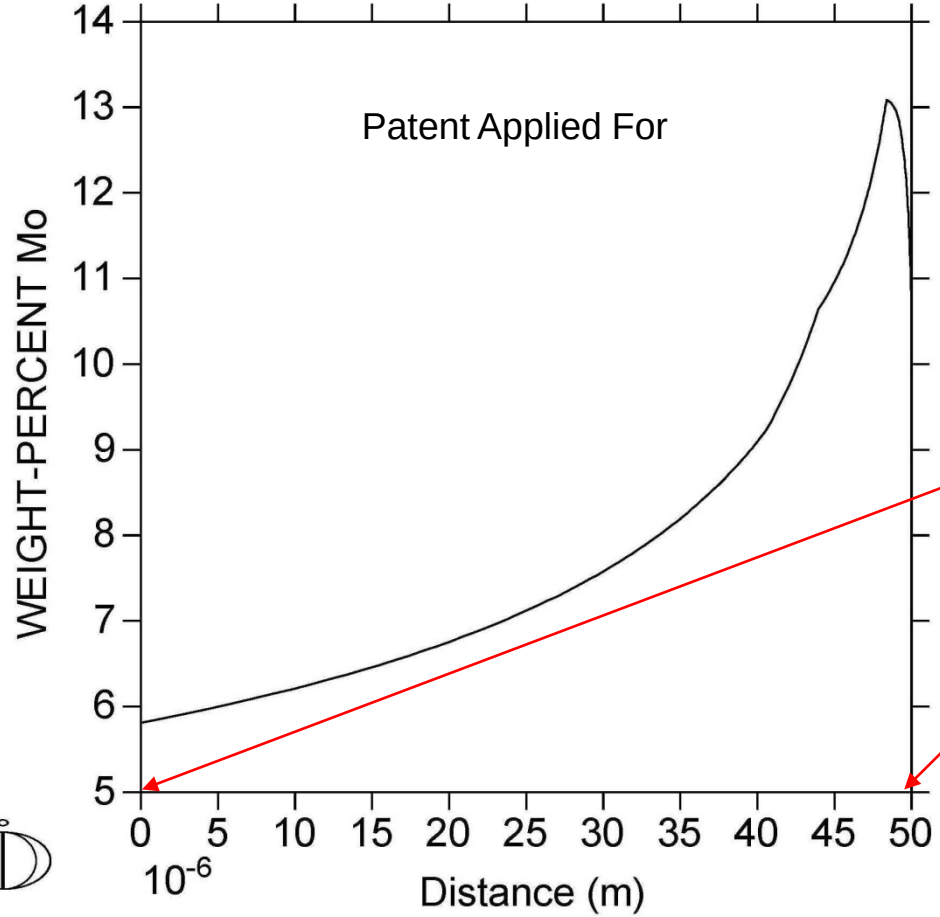
“Enhanced” Slow Cooling

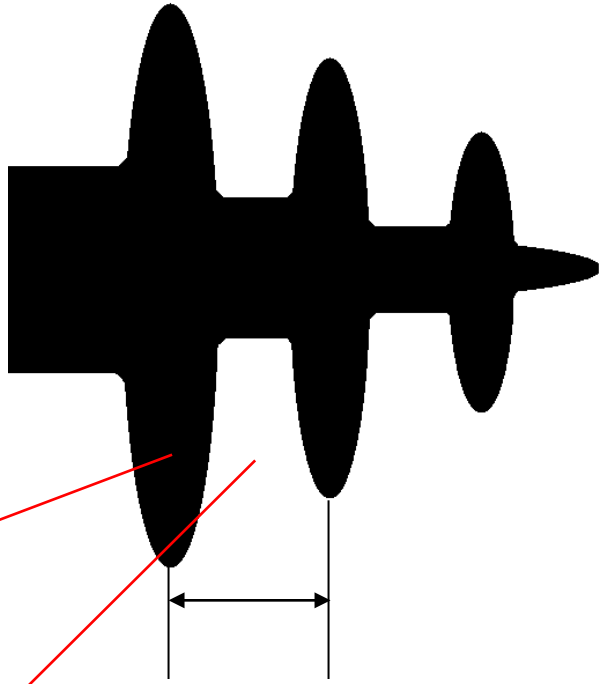




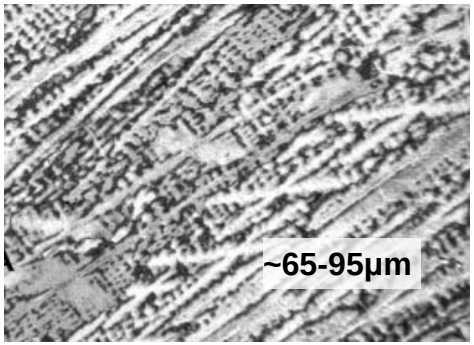
Our casting layout is shown schematically in cross section on the left. A permanent graphite mold was used. This mold was surrounded by loose sand such that the top of the casting was below the sand line. This is our attempt to emulate the “semi-infinite” plate model of the turbine casing.

Segregation Within the FCC Phase

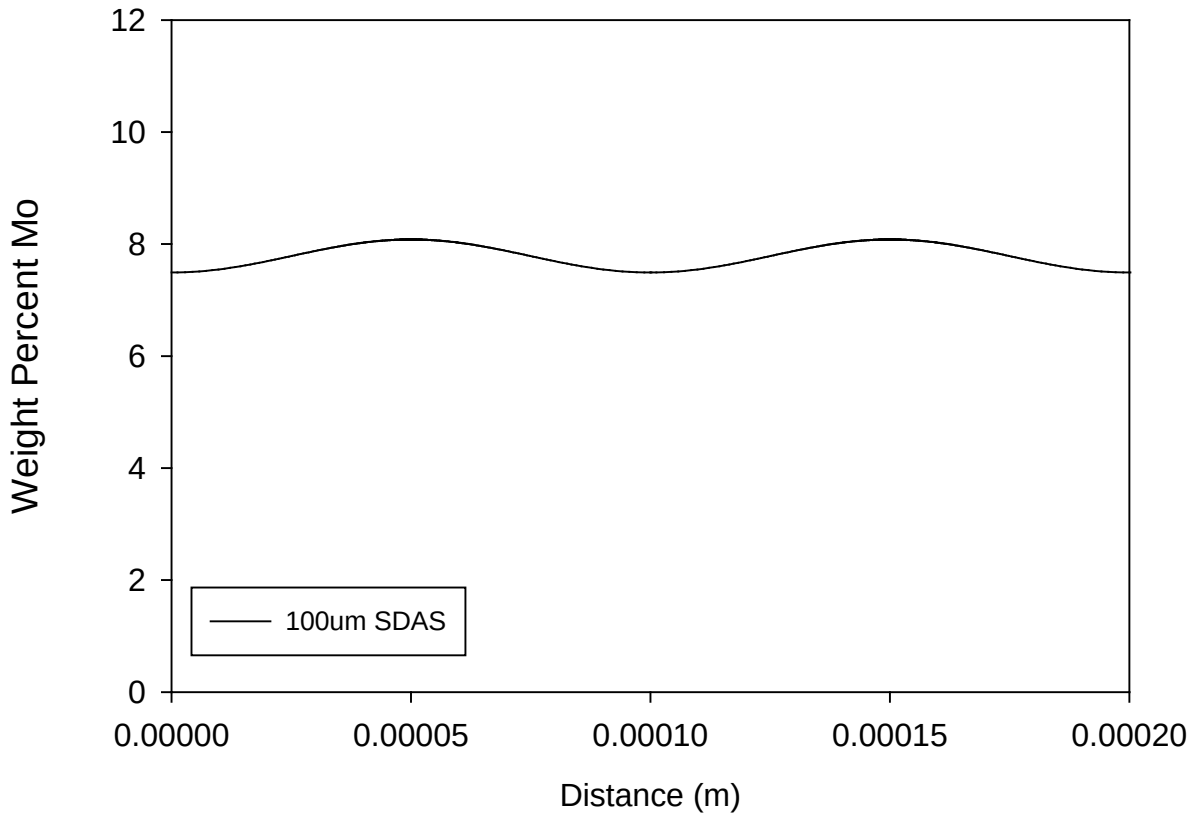




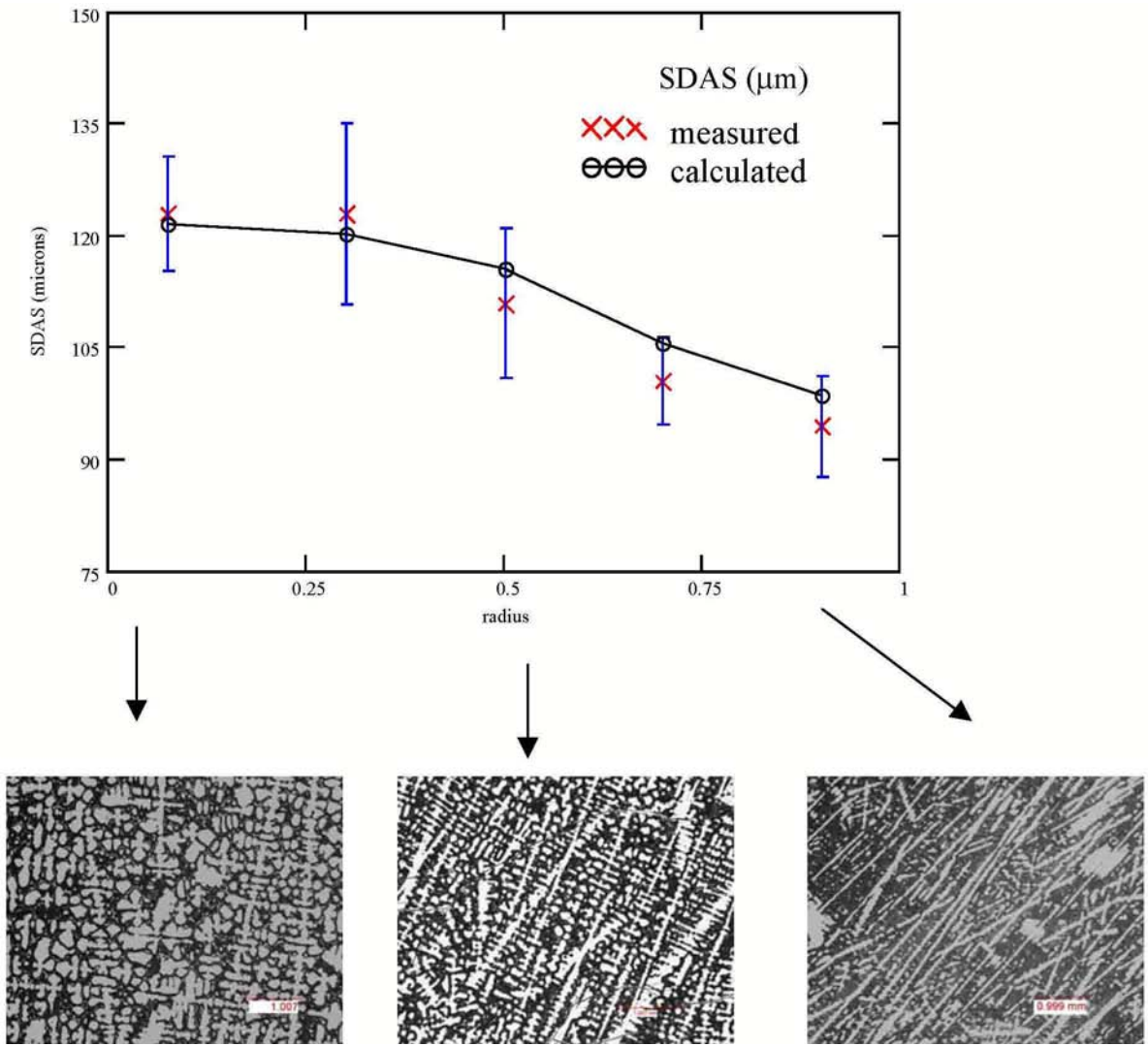
Secondary Dendrite Arm Spacing



Remnant Segregation After Homogenization

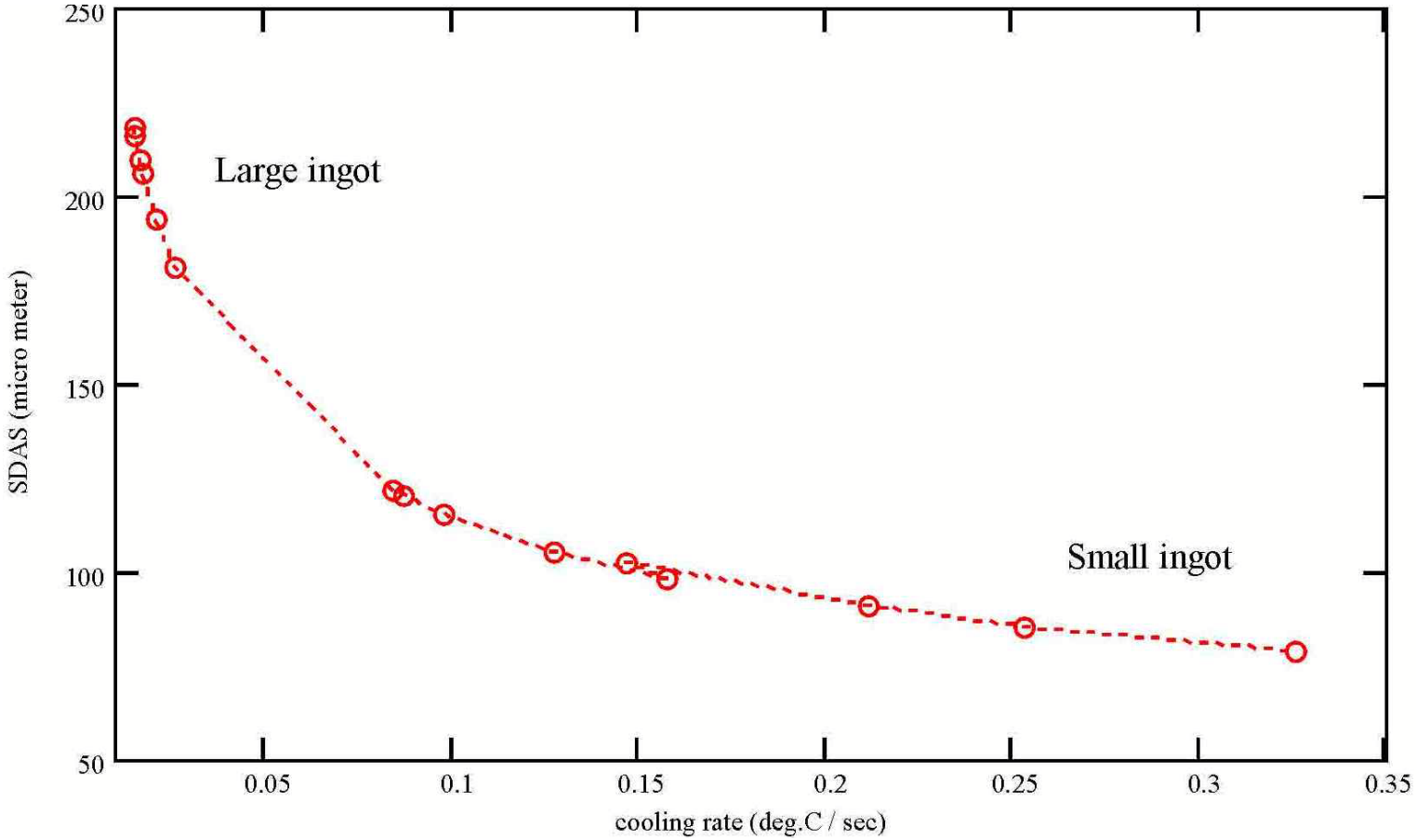


SDAS—Effect of Position



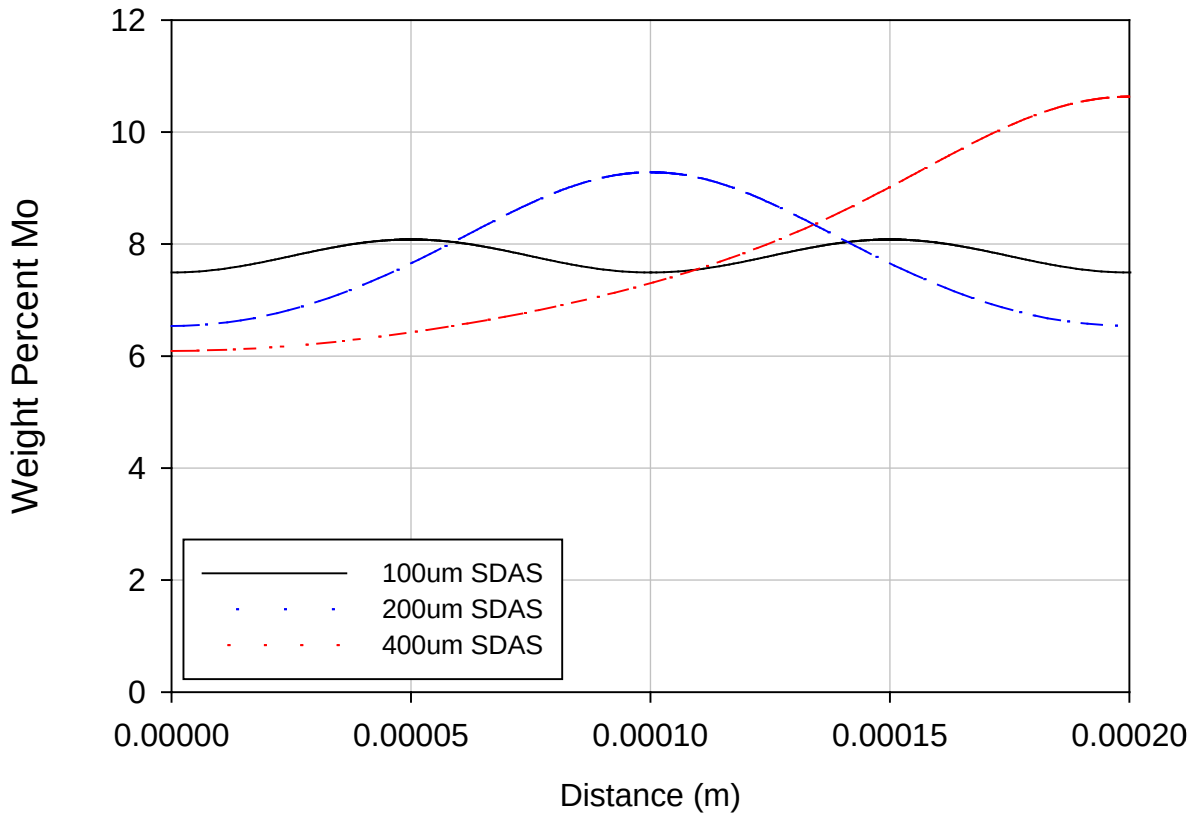
Patel and Murty, 718 conf. (2000)

SDAS—Effect of Cooling Rate

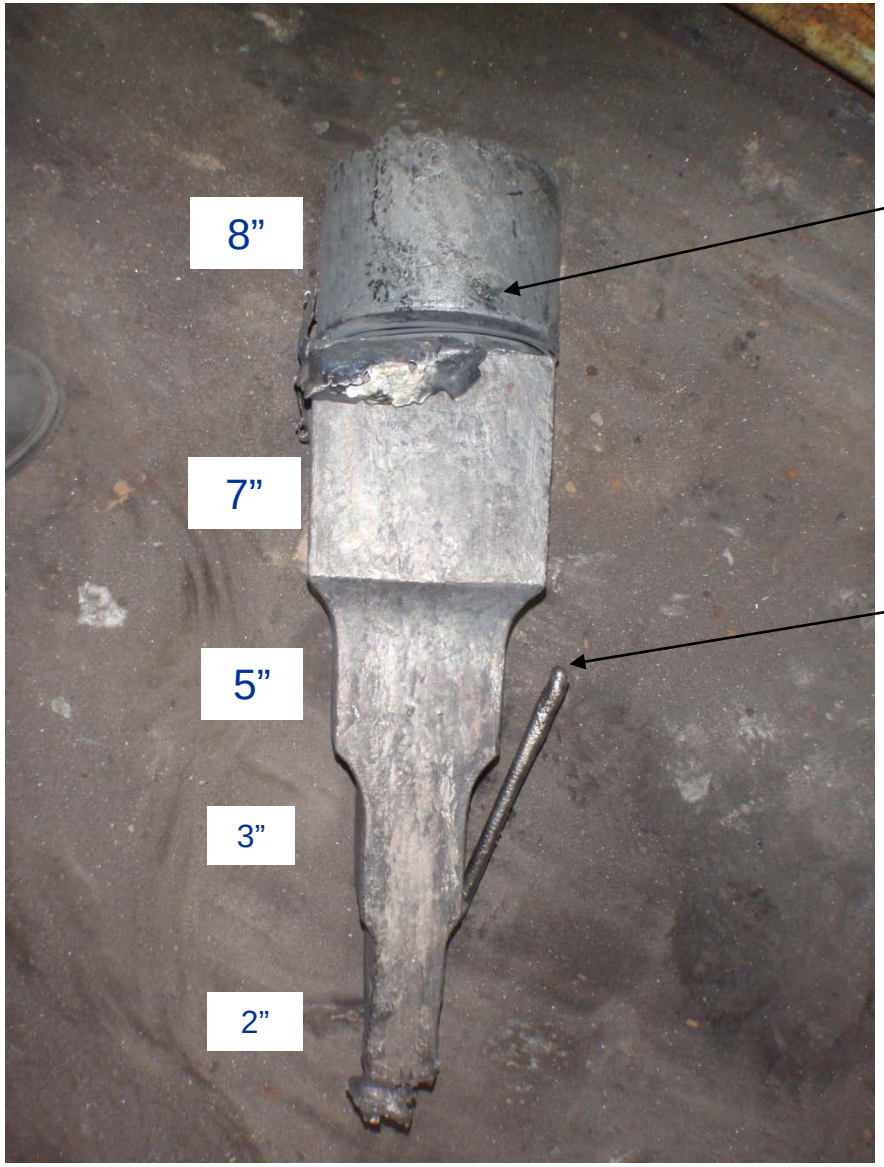


Patel and Murty, 718 conf. (2000)

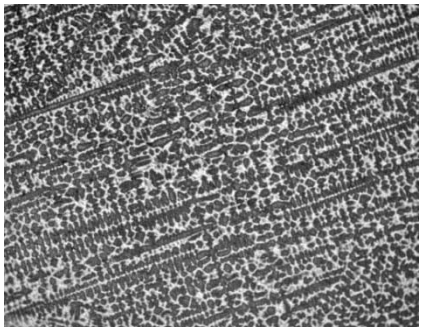
Effect of SDAS on Homogenization



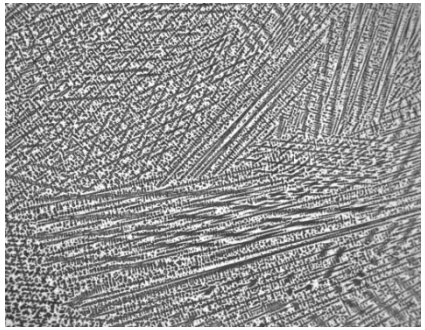
SDAS in Larger Casting



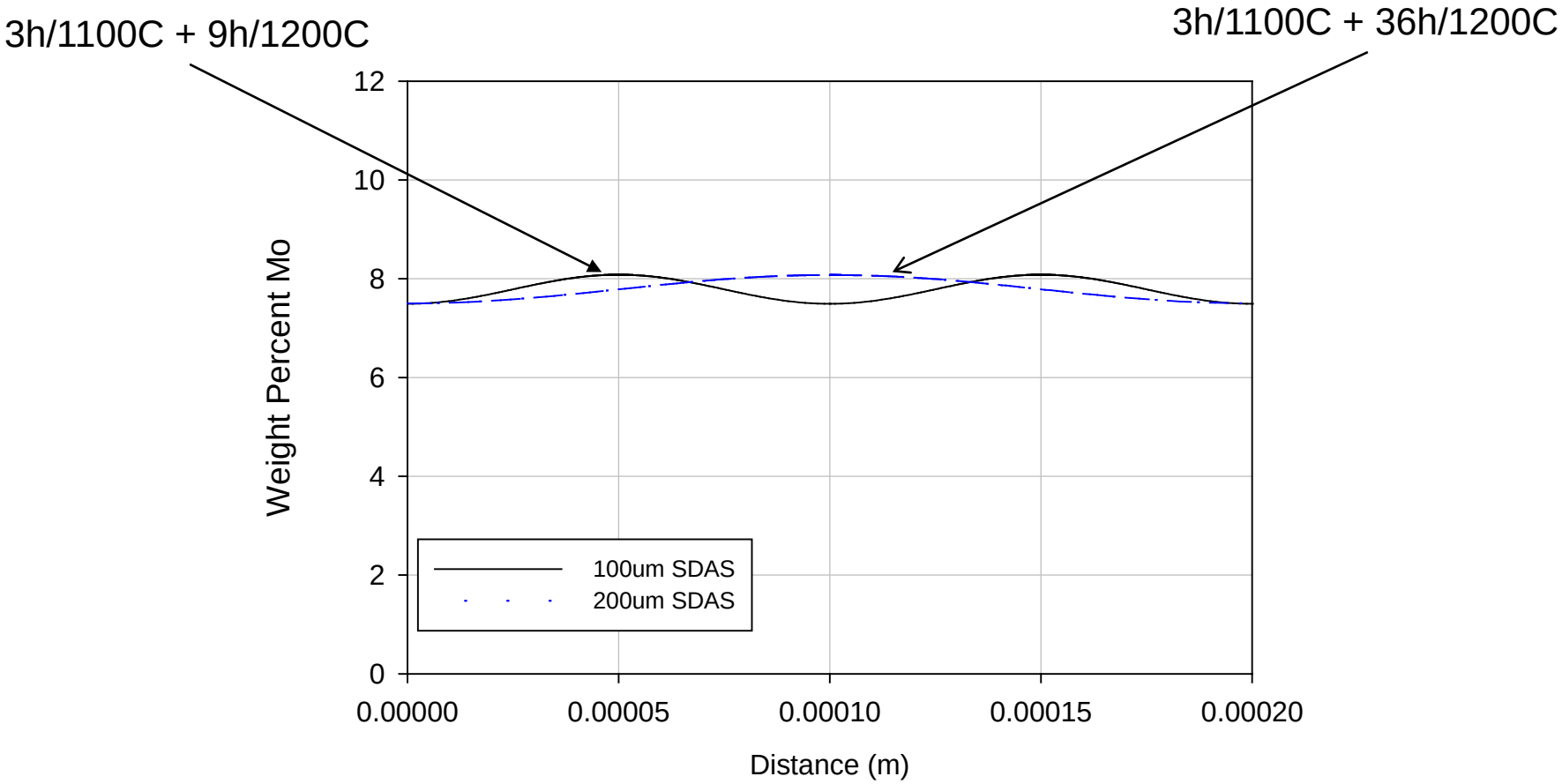
Riser Pad SDAS: 154-188µm



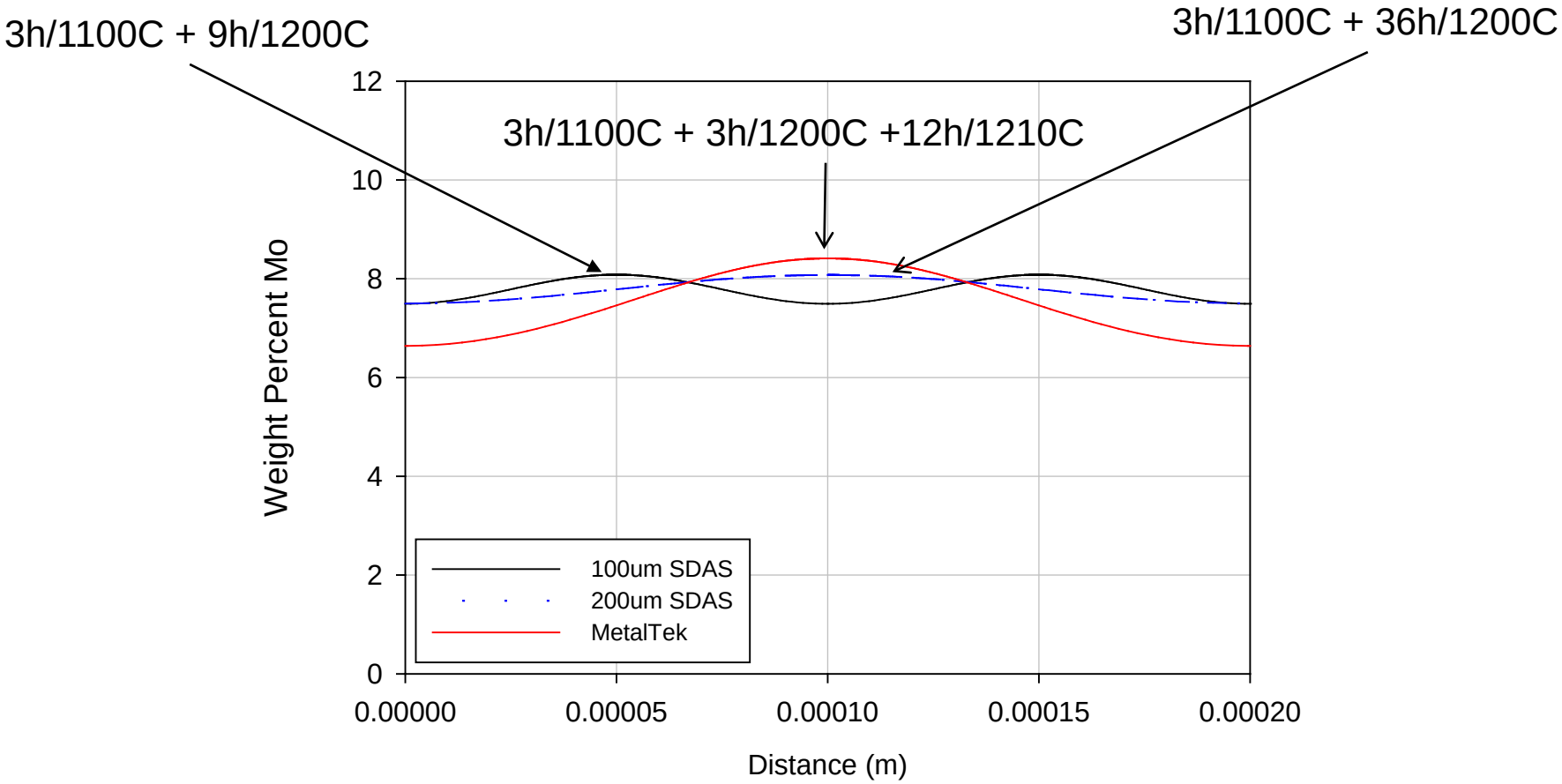
Keel Block SDAS: 57-67µm



Adjusting of Scale of Microstructure



Application to the Casting



Patent Applied For

Residual Mo Segregation

		Minimum (%)	Maximum (%)
As-Cast	Predicted		
	Measured	89	127
Long time HT	Predicted	94	106
	Measured	94	101
HT Applied	Predicted	91	109
	Measured	92	111

Section Summary: As-Cast Profiles

- The refractory elements W, Mo, and Nb do not homogenize after ~22h/1100C
- Significant segregation of the second phase strengthening elements Al, Ti and Nb were observed in many alloys…to the point that 1/2-2/3 of the casting would be considered “lean”.
- In some cases, Cr poor regions are predicted.
- Significant Co segregation was observed in some alloys.
- Significant partitioning of Mn and Si to the interdendritic region was predicted. This result suggests that a turn down in the levels of these elements may be beneficial (e.g., welding).
- Computational Homogenization: Patent applied for.

The Issue of Sulfur

- **Sulfur is detrimental in Ni-based superalloys**
  - Reduces oxide scale adhesion
  - Reduces grain boundary strength
  - Reduces weldability
- **Sulfur content of our alloys typically has been ~100ppm.**
- **The majority of the sulfur comes from Cr additions; a secondary source is Co.**
- **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]

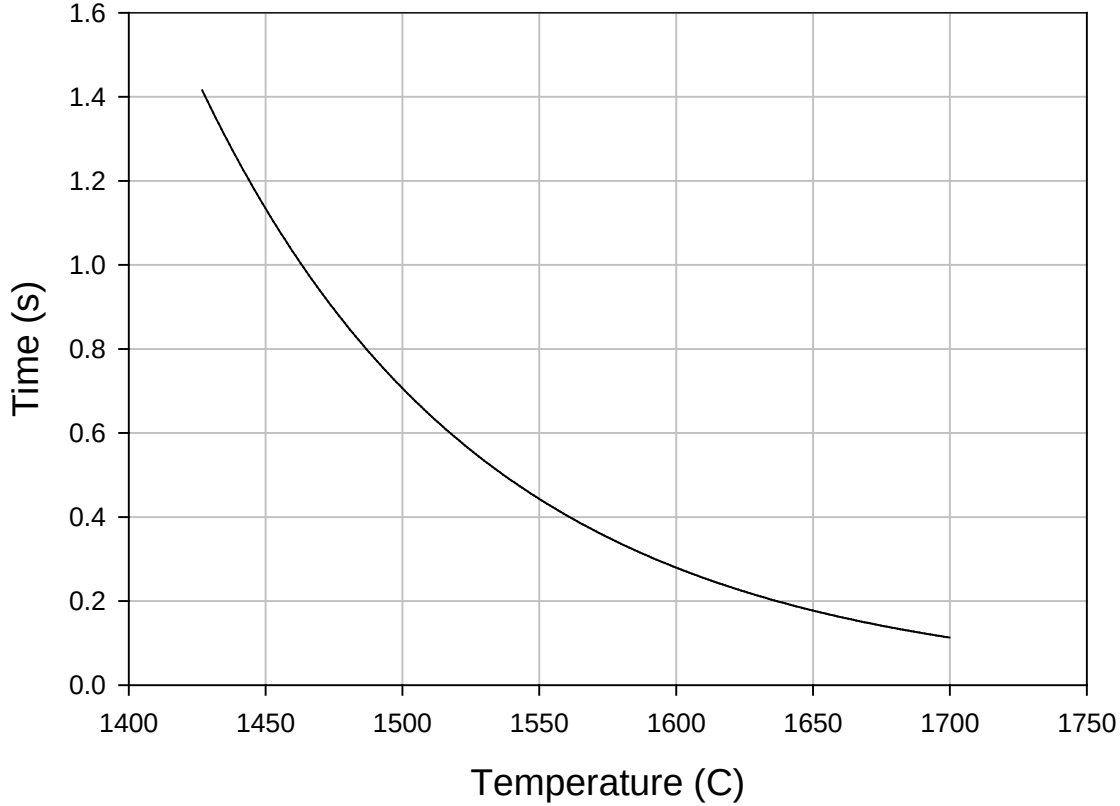
RT = gas constant times absolute temperature [erg/mole = $g.cm^2$/mole]

M = molecular weight of element [g/mole]

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

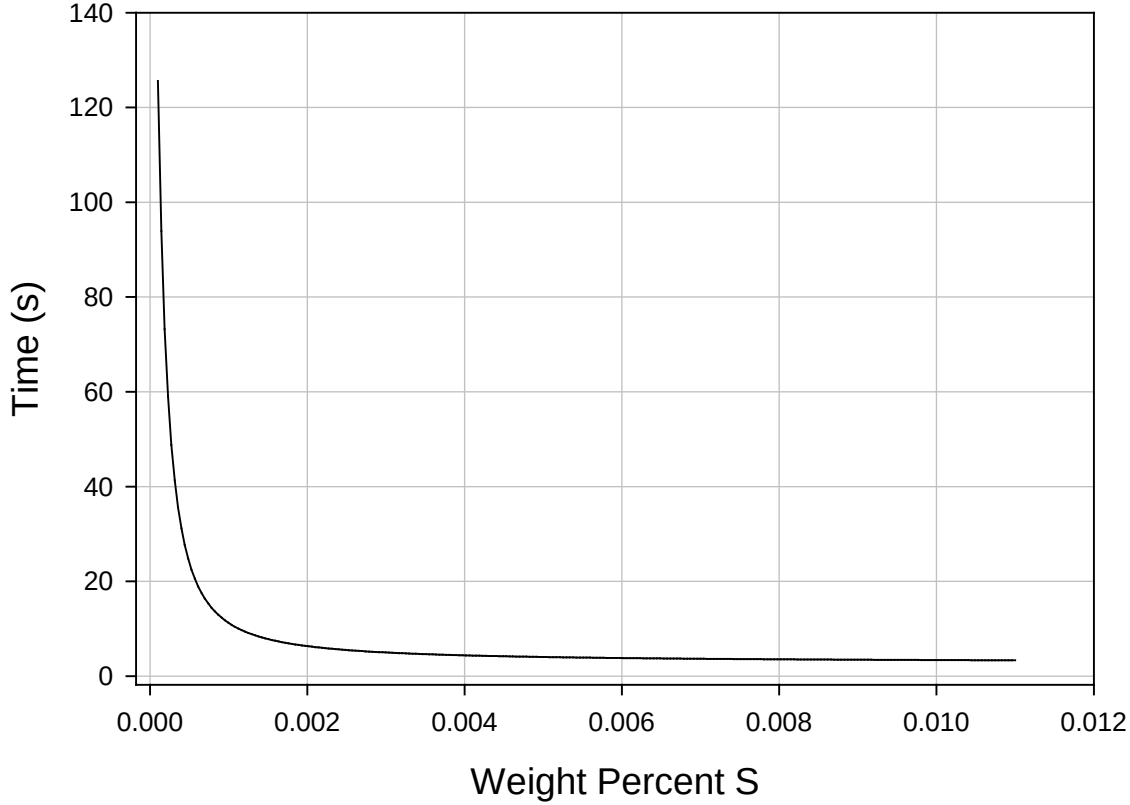
P = partial pressure of pure element at temperature [Pa = g/($cm.s^2$)]

Predicted Time Based on Temperature



100ppm S

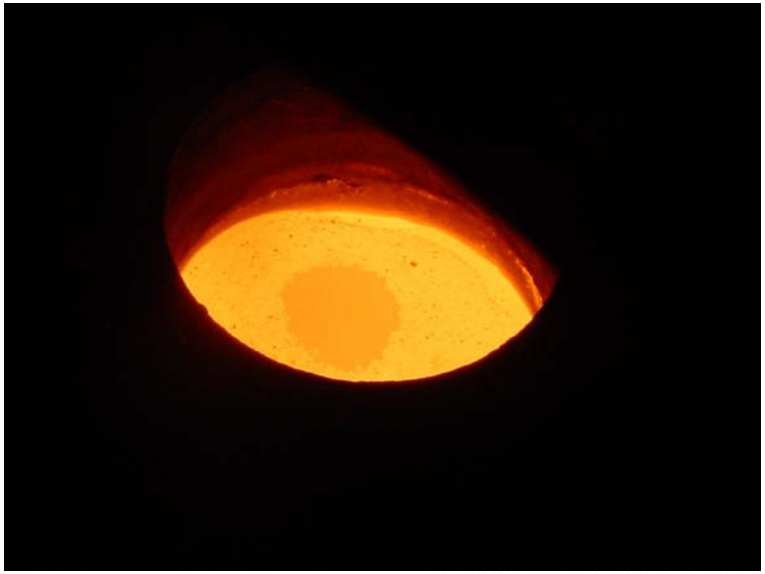
Effect of Changing Composition



Initial Experiments to Reduce Sulfur

Conditions	Results
• T_l+100C/10 minutes	• 41 ppm S
• T_l+100C/20 minutes	• 39 ppm S
• T_l+100C/60 minutes	• 43 ppm S
• T_l+50C/20 minutes	• 43 ppm S
• T_l+100C/20 minutes	• 39 ppm S
• T_l+150C/20 minutes	• 43 ppm S

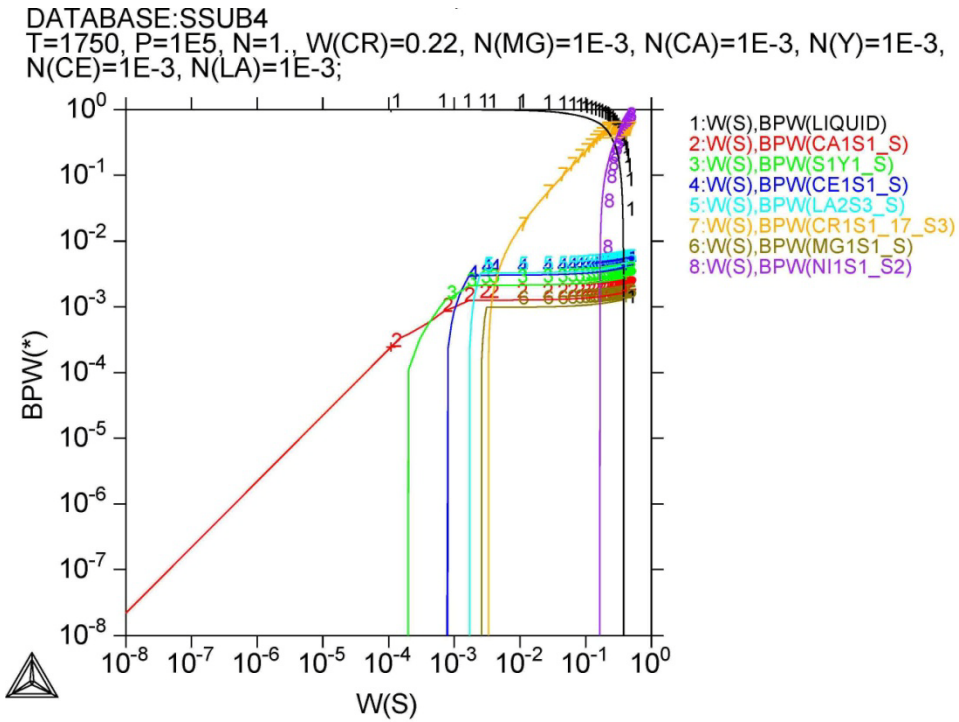
Ni22Cr



Evaluate Sulfur Control on Ni-base alloy

Vacuum distillation of S proved to be impractical.

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, Ca, Y, La, and Ce at 1477°C.



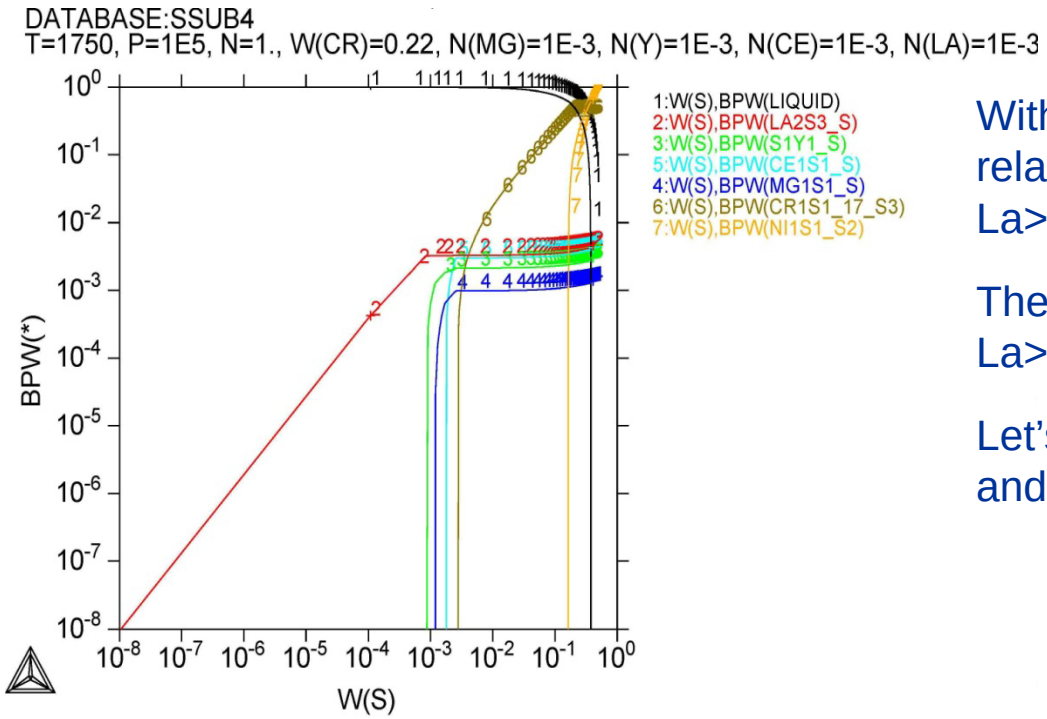
Below ~0.325 w/o S, the ranking in the relative amount of sulfides formed is: La>Ce>Y>Ca>Mg.

The critical S level ranking is as follows: Ca>Y>Ce>La>Mg.

Mg is the lowest rank while there is no clear winner. Let's take Ca out (does not form as much sulfide).

Evaluate Sulfur Control on Ni-base alloy

Now consider 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 (i.e., no Ca) 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.

Let's go on to do experiments using La, Y and Mg.

Verify S model via casting trials in the laboratory.

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. Anecdotally, S removal with Y has been successful on more complicated alloys.

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
Large melt	95	4 La
Ni-30Cr30Co		
NiCrLa	161	321 La
NiCrLa	7	97 La

Section Summary

- Sulfur is detrimental to Ni based superalloys.
- Our sulfur comes mainly from the Cr addition.
- Theoretically, sulfur can be reduced by vacuum distillation or gettering by elemental additions.
- Initial experiments have shown both the be effective.
- Experiments will continue in order to refine these methods.

Disclaimer

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Summary

- A-USC conditions will require advanced Ni-based alloys to operate.
- 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 (patent applied for).
- The performance of these alloys, especially creep, looks promising and is comparable to the wrought analogue.
- The alloys appear to have adequate fluidity for casting.

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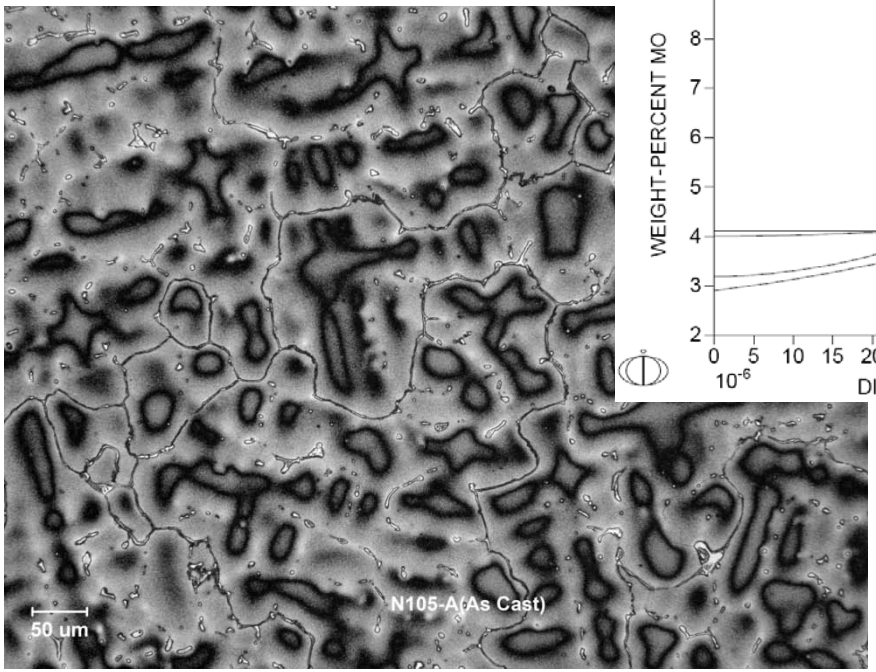
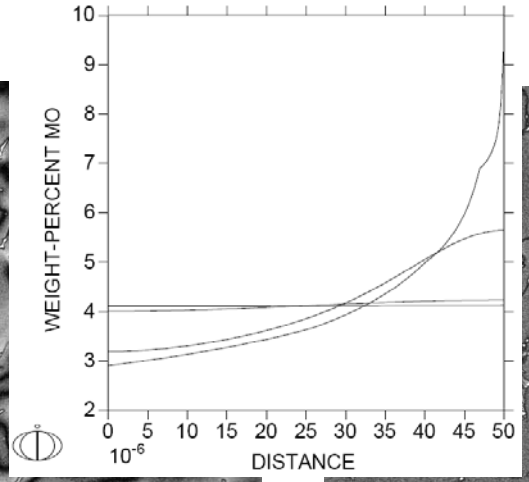
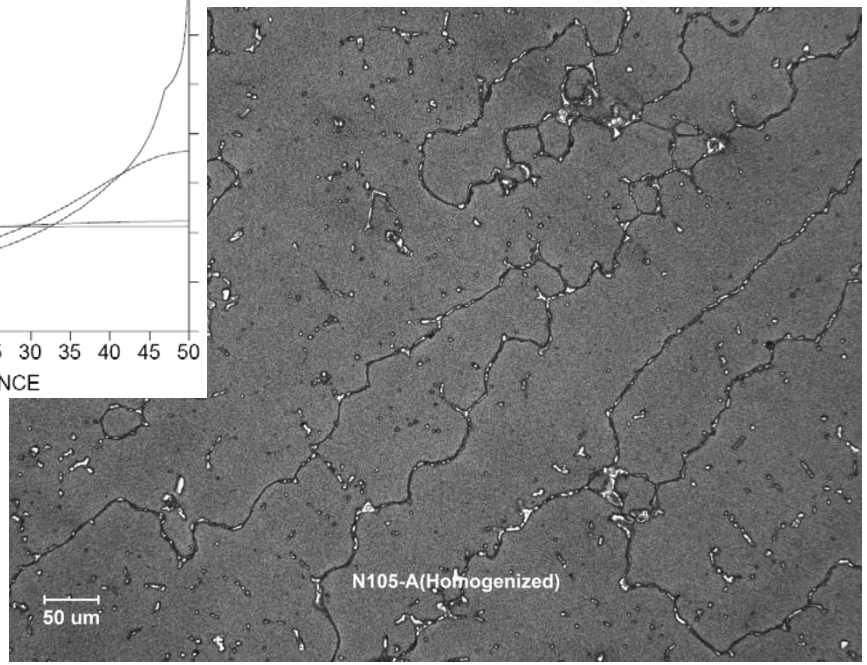
Qualitative Confirmation of the Effectiveness of the Homogenization Heat Treatment







As-Cast

Homogenized

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

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