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Grain refinement of Al-Si alloys by Nb-B inoculation

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Outline

• Grain refinement in Al alloys with Al-5Ti-B

• Concept development

• Application to Al-Si cast alloys

• Al-Nb-B master alloy

• Comparative study between Al-Nb-B and Al-5Ti-B master alloys
ALUMINIUM ALLOYS

PROPERTIES
- LOW DENSITY, 2.7 g/cc
- GOOD MECHANICAL PROPERTIES
- HIGH CORROSION RESISTANCE
- HIGH THERMAL CONDUCTIVITY
- LOW ELECTRICAL RESISTIVITY

ALLOYS

WROUGHT

CAST (Al-Si)

IMPROVEMENT
- FLUIDITY/CASTABILITY
- MACHINABILITY
- CHEMICAL HOMOGENEITY
- MECHANICAL PROPERTIES
- SURFACE QUALITY
- REDUCED SHRINKAGE POROSITY

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Factors determining grain size in as cast microstructure

Nucleation & Growth

Heterogeneous nucleation
Homogeneous nucleation

Growth Kinetics
- Temperature
- Atmosphere/Pressure
- Growth restriction
- Fragmentation
- Cooling rate

\[ \Delta T = T_L - T_g \]
EFFICIENT HETEROGENEOUS NUCLEATION SITES

1. High melting Temp

2. Low lattice mismatch
   (atom position matching)

3. Chemical stability
   (should not react with alloying elements)

GRAIN REFINEMENT:  Al-Ti-B
  Al-Ti-C

  TiB₂ & Al₃Ti

• Orientation Relationships
  \{111\}Al//\{112\}Al₃Ti//\{001\}TiB₂
  \langle110\rangle Al//\langle201\rangle Al₃Ti
  \langle110\rangle Al₃Ti//\langle110\rangle TiB₂

MODIFICATION:  Sr modification of the Si morphology

P to nucleate the primary Si particles

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Influence of Al-Ti-B grain refiner for Al-Si alloys

Ti reaction with Si in Al-Si alloys

Ti is consumed by the formation of TiSi$_2$ and TiSi


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Analogy between Al-Ti & Al-Nb phase diagrams

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## Lattice Mismatch

### Aluminium
- **Element**: Al
- **Phase**: Al
- **Melting Point [°C]**: 660
- **Density [g/cm³]**: 2.70
- **Lattice structure**: Face-Centred Cubic
  - Lattice parameter: \( a = 4.050 \text{ Å} \)

### Titanium
- **Element**: Ti
- **Phase**: Ti
- **Melting Point [°C]**: 1668
- **Density [g/cm³]**: 4.51
- **Lattice structure**: Hexagonal
  - Lattice parameters: \( a = 2.950 \text{ Å}, c = 4.683 \text{ Å} \)

- **Element**: Al₃Ti
- **Phase**: Al₃Ti
- **Melting Point [°C]**: 1350
- **Density [g/cm³]**: 3.36
- **Lattice structure**: Tetragonal
  - Lattice parameters: \( a = 3.848 \text{ Å}, c = 8.596 \text{ Å} \)

- **Element**: TiB₂
- **Phase**: TiB₂
- **Melting Point [°C]**: 3230
- **Density [g/cm³]**: 4.52
- **Lattice structure**: Hexagonal
  - Lattice parameters: \( a = 3.023 \text{ Å}, c = 3.220 \text{ Å} \)

### Niobium
- **Element**: Nb
- **Phase**: Nb
- **Melting Point [°C]**: 2468
- **Density [g/cm³]**: 8.57
- **Lattice structure**: Body-Centred Cubic
  - Lattice parameter: \( a = 3.300 \text{ Å} \)

- **Element**: Al₃Nb
- **Phase**: Al₃Nb
- **Melting Point [°C]**: 1680
- **Density [g/cm³]**: 4.54
- **Lattice structure**: Tetragonal
  - Lattice parameters: \( a = 3.848 \text{ Å}, c = 8.615 \text{ Å} \)

- **Element**: NbB₂
- **Phase**: NbB₂
- **Melting Point [°C]**: 3036
- **Density [g/cm³]**: 6.98
- **Lattice structure**: Hexagonal
  - Lattice parameters: \( a = 3.102 \text{ Å}, c = 3.285 \text{ Å} \)

- **Element**: NbC
- **Phase**: NbC
- **Melting Point [°C]**: 3490
- **Density [g/cm³]**: 7.82
- **Lattice structure**: Face-Centred Cubic
  - Lattice parameter: \( a = 4.430 \text{ Å} \)

**Diagrams**:
- **Al₃Nb**
- **Al (face centred cubic)**
Low Lattice Mismatch – Coherent Interface

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Nb chemical stability with Si

**Nb–Si binary phase diagram**

Temperature, °C

- 2600
- 2400
- 2200
- 2000
- 1800
- 1600
- 1400
- 1200

Nb

Atomic Percent Si

- 0
- 10
- 20
- 30
- 40
- 50
- 60
- 70
- 80
- 90
- 100

Si

Nb, Ti, Si ternary system

- Nb
- Ti
- Si

- Nb5Si3
- Ti5Si3
- Nb3Si

**Nb silicides form at higher temperature than Ti silicides thus preventing poisoning**


J.C. Zhao et al., Materials Science and Engineering A 2004;372:21
Addition of Nb metal powder to liquid Al

Al-Nb 660 °C

Al matrix

Nb particles

Unreacted Nb metallic particulates

750 - 800 °C
Poor dissolution of Nb in liquid Al

Requires high temperature for larger Nb particles and high concentrations

\[ C = C_s \left[ 1 - \exp\left( -\frac{k \cdot s \cdot t}{v} \right) \right] \]

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Addition of Nb fine metal powder to liquid Al

 Nb- Superconductivity – 9K
To verify the Nb dissolution, magnetic moment vs temperature measured

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EFFECT OF Nb on CP Al

CP-Aluminium

700ºC

Al with Nb-B

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COMPARISON OF Al-Ti-B AND Nb-B ON CP Al

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COMPARISON OF Al-Ti-B AND Nb-B TO HYPOEUTECTIC BINARY Al-Si Alloys

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COMPARISON OF Al-Ti-B AND Nb-B TO HYPOEUTECTIC BINARY Al-Si Alloys

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Al-Si alloys for automotive applications

**Engine & transmission Components**
Crankcases
Cylinder heads
Intake manifolds
Housings manual/automatic transmissions
Housings power transfer units

**Chassis Components**
Subframes Knuckles
Steering housings

**Structural Components**
Body structures
Instrument panels
Door frames

**Wheels**
Undercooling for Al-10Si alloy

Al-10 Si alloy cooling curve

$\Delta T_{\text{Ref}} = 2.1^\circ\text{C}$

$T_{\text{nucl}} = 594^\circ\text{C}$

$T_{\text{min}} = 590.3^\circ\text{C}$

$T_g = 592.4^\circ\text{C}$

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Grain size up to 1 cm

Reference

$\Delta T_{Ref} = 2.1^\circ C$

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Undercooling in the presence of NbB$_2$/Al$_3$Nb

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Grain structure

Reference: Grain size up to 1 cm

Nb-B: Grain size: 2-3 mm

$\Delta T_{\text{Ref}} = 2.1^\circ C$

$\Delta T_{\text{Nb-B}} = 1.3^\circ C$
Cooling curves for Al-11Si (LM6) alloy

a) Cooling curve for LM6 alloy:

- $T_{\text{nucl}} = 588.0 \, ^\circ\text{C}$
- $T_g = 587.0 \, ^\circ\text{C}$
- $\Delta T = 2.5 \, ^\circ\text{C}$
- $T_{\text{rec}}$
- $T_{\text{min}} = 584.5 \, ^\circ\text{C}$

b) Cooling curve for LM6 + Nb-B alloy:

- $T_{\text{nucl}} = 588.8 \, ^\circ\text{C}$
- $T_g = 587.5 \, ^\circ\text{C}$
- $\Delta T = 0.7 \, ^\circ\text{C}$
- $T_{\text{min}} = 586.8 \, ^\circ\text{C}$

LM6 with Grain refiner addition

LM6
Hypereutectic Binary Al-Si Alloys

Al-14Si

200 µm

α-Al dendrite

700°C

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Hypereutectic Binary Al-Si Alloys - Eutectic

Al-16Si

Al-18Si

Al-27Si

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Hypereutectic Binary Al-Si Alloys – Primary Si

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Application of Nb-B grain refiner to Al-Si commercial alloys
## Commercial alloys tested with Nb-B

<table>
<thead>
<tr>
<th>GB</th>
<th>USA</th>
<th>Si</th>
<th>Mg</th>
<th>Mn</th>
<th>Cu</th>
<th>Ni</th>
<th>Zn</th>
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<tbody>
<tr>
<td>LM6</td>
<td>A413</td>
<td>10.0-13.0</td>
<td>0.1max</td>
<td>0.5max</td>
<td>0.1max</td>
<td>0.1max</td>
<td>0.1max</td>
<td>0.6max</td>
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<tr>
<td>LM13</td>
<td>336</td>
<td>10.0-13.0</td>
<td>0.2-0.4</td>
<td>0.5max</td>
<td>0.7-1.5</td>
<td>1.5max</td>
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<td>LM24</td>
<td>A380</td>
<td>7.5-9.5</td>
<td>3 max</td>
<td>0.5max</td>
<td>3.0-4.0</td>
<td>0.5</td>
<td>3</td>
<td>1.3max</td>
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<tr>
<td>LM25</td>
<td>A356</td>
<td>6.5-7.5</td>
<td>0.2-0.6</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>GB</th>
<th>USA</th>
<th>Si</th>
<th>Mg</th>
<th>Mn</th>
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<th>Ni</th>
<th>Zn</th>
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<tbody>
<tr>
<td></td>
<td>9.99</td>
<td>A413</td>
<td>0.005</td>
<td>0.005</td>
<td>0.0017</td>
<td>0.0044</td>
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<td>10.98</td>
<td>A380</td>
<td>0.268</td>
<td>0.21</td>
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<td>0.068</td>
<td>0.778</td>
<td>0.83</td>
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<td>6.06</td>
<td>A356</td>
<td>0.275</td>
<td>0.265</td>
<td>2.725</td>
<td>0.0257</td>
<td>0.305</td>
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<td>11.9</td>
<td>A356</td>
<td>0.8</td>
<td>0.005</td>
<td>3.7</td>
<td>2</td>
<td>0.003</td>
<td>0.12</td>
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Nb-B Grain Refiner for Al-Si cast alloys

- Highly effective for Al-Si alloys & Mg alloys
- Fine & uniform grain structure
- Grain size is less sensitive to cooling rate
- Highly effective in sand casting cooling conditions
- Reduced porosity & macro defects
- Fine eutectic structure & intermetallics
- Improved ductility & strength
- Tolerant to Fe contamination
- Recycling of Al-Si scrap
COMMERCIAL HYPOEUTECTIC Al-Si ALLOYS

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Nb-B Grain Refiner for Al-Si cast alloys

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  - Grain size is less sensitive to cooling rate
  - Highly effective in sand casting cooling conditions
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Porosity

Al-11Si (LM6) no addition
~200 µm
~1200 µm

Al-11Si (LM6) with Nb-B
~160 µm
~200 µm

10 mm

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Al-Nb-B Grain Refiner for Al-Si cast alloys

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Effect of Cooling Rate

- 20 mm
- 20 mm
- 20 mm
- 700ºC

- α-Al grain size [µm]
- Cooling rate [°C/s]

- LM6 (Reference)
- LM6 + Nb-B
- LM25 (Reference)
- LM25 + Nb-B
EFFECT OF COOLING RATE

\[
d = 2072 \left( \frac{dT}{dt} \right)^{-0.34}
\]

\[
d = 514 \left( \frac{dT}{dt} \right)^{-0.14}
\]

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Effect of Cooling Rate

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 Nb-B Grain Refiner for Al-Si cast alloys

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Al-Nb-B ADDITION

Al-9Si-2Cu-0.7Mg-0.15Fe
### A354

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Condn.</th>
<th>%Cu</th>
<th>%Mg</th>
<th>%Si</th>
<th>%Fe</th>
<th>%Mn</th>
<th>%Ni</th>
<th>%Zn</th>
<th>%Pb</th>
<th>%Sn</th>
<th>%Ti</th>
<th>%Sr</th>
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<tbody>
<tr>
<td>A354</td>
<td>CAST</td>
<td>1.60-2.0</td>
<td>0.50-0.60</td>
<td>8.6-9.44</td>
<td>0.154</td>
<td>0.05-0.10</td>
<td>0.054</td>
<td>0.10</td>
<td>0.014</td>
<td>0.054</td>
<td>0.10-0.154</td>
<td>0.02-0.030</td>
</tr>
</tbody>
</table>

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Al-Nb-B Grain Refiner for Al-Si cast alloys

- Highly effective for Al-Si alloys & Mg alloys
- Fine & uniform grain structure
- Grain size is less sensitive to cooling rate
- Highly effective in sand casting cooling conditions

**Reduced porosity & macro defects**
- Fine eutectic structure & intermetallics
- Improved ductility & strength
- Tolerant to Fe contamination
- Recycling of Al-Si scrap

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Reduced Macro-porosity with Nb-B

Al-11Si (LM6)

with Al-5Ti-B

with Nb-B

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Aluminium Al-Ti-B Novel grain refiner

Reduced porosity in Nb-B grain refiner added castings

Tp1 test 700 °C
Al-7Si alloy

Without

With Nb-B addition

Fine grain structure
Reduced porosity
Nb-B Grain Refiner for Al-Si cast alloys

- Highly effective for Al-Si alloys & Mg alloys
- Fine & uniform grain structure
- Grain size is less sensitive to cooling rate
- Highly effective in sand casting cooling conditions
- Reduced porosity & macro defects

**Fine eutectic structure & intermetallics**

- Improved ductility & strength
- Tolerant to Fe contamination
- Recycling of Al-Si scrap
Fine eutectic structure

Al-11Si (LM6) with Nb-B
Finer Eutectic Si - wider range of cooling rates
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Reference (Al-13Si) with Nb-B
Nb-B Grain Refiner for Al-Si cast alloys

- Highly effective for Al-Si alloys & Mg alloys
- Fine & uniform grain structure
- Grain size is less sensitive to cooling rate
- Highly effective in sand casting cooling conditions
- Reduced porosity & macro defects
- Fine eutectic structure & intermetallics

**Improved ductility & strength**

- Tolerant to Fe contamination
- Recycling of Al-Si scrap

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Improved strength & ductility

Al-11Si alloy

UTS [MPa]

Elongation [%]

Gravity mould
Melting temp: 800 °C
Casting temp: 800 °C

Machined from cast bars

Improved
• Crash performance
• Fatigue performance

yield
82.4 Mpa → 102 Mpa

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Al-13Si piston alloy

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Nb-B Grain Refiner for Al-Si cast alloys

- Highly effective for Al-Si alloys & Mg alloys
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- Highly effective in sand casting cooling conditions
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- Improved ductility & strength

- Tolerant to Fe contamination
- Recycling of Al-Si scrap
Control of Fe-intermetallics in Al scrap

Grain refiner to control Al-Fe-Si intermetallics

Al-Fe-Si large needle structure detrimental to mechanical properties
Recovery of properties in Fe-rich aluminium scrap

Properties recovery through refinement of intermetallics

Virgin alloy with 1 wt% Fe impurity

Reduced properties due to larger, needle structured intermetallics

Virgin alloy

UTS (MPa) vs Elongation, 4D (%) graph
Nb-B Grain Refiner for Al-Si cast alloys

- Highly effective for Al-Si alloys & Mg alloys
- Fine & uniform grain structure
- Grain size is less sensitive to cooling rate
- Highly effective in sand casting cooling conditions
- Reduced porosity & macro defects
- Fine eutectic structure & intermetallics
- Improved ductility & strength
- Tolerant to Fe contamination

Re-melting & Fading study
FADING STUDY

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REQUIRED TIME TO SEDIMENT/FADE

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Remelting

Al-9Si-1.5Cu-0.6Mg-0.15Fe / RE-MELT

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MASTER ALLOY DEVELOPMENT
Al-Nb-B Master Alloy

1. Nb metallic powder + KBF4

2. Addition of Nb metallic powder to diluted Al-B master alloy
MASTER ALLOY (METHOD 1)

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Al-4Nb-1B on LM25

Reference

680°C

NB-B (M.A.)

Al-Nb-B (powders)
Al-4Nb-1B on LM6

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Al-2Nb-1B on Al-10Si
EFFECT OF Al-2Nb-2B ON UNDERCOOLING FOR COMMERCIAL Al-Si ALLOYS

<table>
<thead>
<tr>
<th>Material</th>
<th>Si content [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7</td>
</tr>
<tr>
<td>Reference</td>
<td>$\Delta T_\alpha$</td>
</tr>
<tr>
<td></td>
<td>$\Delta T_{eu}$</td>
</tr>
<tr>
<td>Al-2Nb-2B master alloy addition</td>
<td>$\Delta T_\alpha$</td>
</tr>
<tr>
<td></td>
<td>$\Delta T_{eu}$</td>
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</table>
EFFECT OF Al-2Nb-2B ON COMMERCIAL Al-Si ALLOYS

HYPO-EUTECTIC ALLOYS (LM24/25)

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EFFECT OF Al-2Nb-2B ON COMMERCIAL Al-Si ALLOYS

PISTON ALLOY (HYPER-EUTECTIC: 13 wt.% Si)
EFFECT OF Al-2Nb-2B ON COMMERCIAL Al-Si ALLOYS

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740 °C
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**Effect of Al-2Nb-2B on Commercial Al-Si Alloys**

- **α-Al grain size [µm]**
- **Cooling rate, \(dT/dt\) [°C/s]**
- **Si content**

![Graph showing the effect of Al-2Nb-2B on commercial Al-Si alloys with varying Si content and cooling rates.](image-url)
Columnar grain structure

Fine (<0.5mm) equiaxed grains

Chill zone

Al-10 Si alloy - Direct Chill Cast Billets

Reference with Al-Nb-B

Equiaxed
Al-10Si DC billets

Zone 1: chilled zone
Zone 2: columnar crystals
Zone 3: long columnar crystals
Zone 4: equiaxed crystals

Reference
Inoculated Nb-based compounds as heterogeneous nuclei

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Comparative study between Al-Nb-B and Al-5Ti-B master alloys
Comparison between Ti-B and Nb-B

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GRAIN REFINEMENT EFFICIENCY COMPARISON

WHEEL ALLOYS (HYPOTECTIC: 7 wt.% Si)

740°C

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Summary

• Nb-B addition to Al-Si melt refines the grain structure of casting

• End-user benefits:
  • Improved strength & ductility
    ✓ Lighter/thinner structures
  • Homogeneous properties (thick & thin sections)
    ✓ Complex structures
  • Tolerant to Fe contamination
    ✓ Closed loop recycling of scrap containing higher Fe
  • Reduced shrinkage porosity - Improved soundness
    ✓ Component rejection ratio can be minimised