INFLUENCE OF HIGH ENERGY BALL MILLING ON REACTIVITY IN Ni-AL GASLESS HETEROGENEOUS SYSTEM
Motivation of the Research

Reactive exothermic mixtures of nickel and aluminum may be applied for

- chemical energy storage,
- nano-scale energetic devices
- materials synthesis and other applications

Microstructural control
- high energy ball milling (HEBM)
- production of multilayer nano-foils, etc

Ignition temperature ($T_{ig}$) - the lowest ambient temperature at which the self-propagating reaction initiates.
Effect of HEBM on the reactivity of Ni-Al system

Initial Ni + Al mixture

Ni ≈ 5 μm

Al ≈ 20 μm
<table>
<thead>
<tr>
<th>Milling conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Planetary mill</td>
<td>Retsch P100</td>
</tr>
<tr>
<td>Stainless steel vial</td>
<td>250ml</td>
</tr>
<tr>
<td>Ball / powder ratio</td>
<td>5:1</td>
</tr>
<tr>
<td>Ball (stainless steel) size</td>
<td>10 mm</td>
</tr>
<tr>
<td>Total wt. of ball during milling</td>
<td>170g</td>
</tr>
<tr>
<td>Rotational speed</td>
<td>300 rpm</td>
</tr>
<tr>
<td>Environment</td>
<td>argon</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Milling</td>
</tr>
<tr>
<td>Dry + Wet Milling</td>
</tr>
</tbody>
</table>

Process controlling agent – Hexane
Microstructural transformations in Ni + Al mechanically treated mixtures
Structural transformation during the Dry ball milling of Ni + Al mixture
Two microstructures in Dry Ball Milled materials

- Pt protective layer
- Intermixed structure
- non-uniform structure
# Two microstructures in Dry + Wet Millings Ni+Al mixtures

<table>
<thead>
<tr>
<th>Mechanical treatment conditions</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>F4</th>
<th>F5</th>
<th>F6</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min DM + 10 min WM</td>
<td>![Image]</td>
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</tbody>
</table>

**Particle sizes by fractions**
- **F1**: Below 25 μm
- **F2**: 25-53 μm
- **F3**: 53-106 μm
- **F4**: 106-355 μm
- **F5**: 355-850 μm
- **F6**: More than 850 μm

**Intermixed structure**

**Non-uniform structure**
Phase Compositions of Ni + Al mixtures

Non-uniform structure

Nano-intermixed structure

Initial mixture

2θ (degree)

Intensity, a.u.

- Ni
- Al

(111)
(200)
(220)
Microstructure of the Ni-Al composite particle

Nano-intermixed structure

non-uniform structure
Non-uniform structure

Nano-intermixed structure
STEM images of Nano-intermixed structure
Reactivity of Ni + Al mechanically treated mixtures
Setup for measuring Ignition temperature of Ni+Al composite particles

Ignition temperature ($T_{ig}$) - the lowest ambient temperature at which the self-propagating reaction initiates.

Temperature – Time Profiles

Heating rate $\approx 100 \, ^\circ C/s$

Ni – Al particles

Special resolution - 5μm
Temperature resolution - 1°C
Recording speed - 1000 frames/s
$T_{IG}$ VS. PARTICLE SIZES OF NI-AL MIXTURE AFTER 0 MIN DM + 10 MIN WM

Particle size, $\mu$m

Intermixed structure

Mix of two structures

Non-uniform structure
$T_{IG}$ OF Ni+Al MECHANICALLY TREATED MATERIALS
### Microstructure – Reactivity Relationship

#### Particle sizes by fractions

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<th>Mechanical treatment conditions</th>
<th>F1 (Below 25 µm)</th>
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<tr>
<td>0 min DM + 10 min WM</td>
<td></td>
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</tr>
<tr>
<td>4 min DM + 10 min WM</td>
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<tr>
<td>8 min DM + 10 min WM</td>
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<tr>
<td>13 min DM + 10 min WM</td>
<td></td>
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<tr>
<td>17 min DM + 10 min WM</td>
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<td></td>
</tr>
<tr>
<td>25 - 53 µm</td>
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#### Intermixed structure

#### Non-uniform structure

![Graph showing T_{lep} temperature vs. particle size (µm) with different conditions and fractions.]

- 0 min DM + 10 min WM
- 4.25 min DM + 10 min WM
- 8.5 min DM + 10 min WM
- 12.75 min DM + 10 min WM
- 17 min DM + 10 min WM

![Histogram showing particle size distribution (µm) with different conditions and fractions.]

- d<25
- 25<d<53
- 53<d<106
- 106<d<350
- 355<d<850
- 850<d
**DTA analysis of Ni + Al mixtures**

Initial mixture

- **650°C**: Al melts

**Temperature, °C**

- **680°C**: heating peak
- **360°C**: 420°C: intermixed structure
- **250°C**: 470°C: non-uniform structure
- **470°C**: 580°C: non-uniform structure

Heating rate = 50 °C/min
DTA analysis of Ni + Al mixtures

Temperature, °C

ΔT

- Non-uniform structure: 470°C, 580°C
- Intermixed structure: 360°C, 420°C, 250°C
Conclusions

• Two types of microstructures (non-uniform and mamo-intermixed) is observed in the Ni+Al composite particles produced by high energy ball milling
• The Ni-Al composite’s microstructure can be tailored by adjusting the milling conditions
• Reactivity of Ni+Al composite particles is primarily depend on the microstructure, and intermixed nanostructure results in very low thermal ignition temperatures (~250°C).