Constitutional Properties of Selected Ternary R-Ni-Al alloys (R= Ce, Sm)

S. Delsante, G. Borzone
The addition of misch metal to aluminium-based alloys improves:

- Tensile strength
- Heat resistance
- Vibration resistance
- Corrosion resistance
- Extrudability

Low-density glassy alloys contain:

- ~ 90 at% Al,
- 5 to 9 at% transition metals (Fe, Co, Ni, Rh)
- ~ 5 at% rare earths (Ce, Nd, Y)

They have:

- High tensile strength
- Crystallization temperature between 250°C and 300°C
- Nanocrystal dispersions of essentially pure Al
- Low density (aerospace industry)

Amorphous phases formed in the La-Ni-Al system (Inoue 1997)

(ASM Gschenidner vol.2, 1990)
<table>
<thead>
<tr>
<th>Title</th>
<th>Authors</th>
<th>Journal/Book</th>
<th>Volume/Issue/Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase relations of the Sm–Ni–Al ternary system at 500 °C in the 40–100 at.% Al region</td>
<td>S. Delsante, R. Raggio and G. Borzone</td>
<td>Intermetalics</td>
<td>16 (11-12), 2008, 1250-1257</td>
</tr>
<tr>
<td>Chemical and thermodynamic properties of several Al–Ni–R systems</td>
<td>G. Borzone, R. Raggio, S. Delsante and R. Ferro</td>
<td>Intermetallics</td>
<td>11 (11-12), 2003, 1217-1222</td>
</tr>
<tr>
<td>Synthesis and Structural Characterization of Ternary Compounds Belonging to the Series $RE_{2+m}$Ni$<em>{4+m}$Al$</em>{15+4m}$ ($RE$ rare earth metal)</td>
<td>S. Delsante, K. W. Richter, H. Ipser and G. Borzone</td>
<td>Z. Anorg. Allg. Chem.</td>
<td>635, 2009, 365-368</td>
</tr>
<tr>
<td>Influence of rare earth metals on the characteristics of anodic oxide films on aluminium and their dissolution behaviour in NaOH solution</td>
<td>F. Rosalbino, S. Delsante, G. Borzone and E. Angelini</td>
<td>Corrosion Science</td>
<td>52 (2), 2010, 322-326</td>
</tr>
</tbody>
</table>
The aim of this work is the investigation of the isothermal sections at 800°C of the R-Ni-Al systems (R= Ce and Sm) in the Al-rich part to underline similarities and differences in the formation of ternary phases and in the established phase relationships.

**Why Ce and Sm?**
Ce represents the light rare earth, Sm is known to have a “boundary behavior” between light and heavy rare earths.

**Outline**
- Literature data on R-Ni-Al systems (R = Ce and Sm)
- Experimental details
- Results and discussion
Three recent publications about the Ce-Ni-Al system:

1. [08Tang]: Experimental investigation of the Al-Ce-Ni system at 800°C (Intermetallics 16, 2008, 432-439)

2. [09Tang]: The phase equilibria of the Al-Ce-Ni system at 500°C (JALCOM 470, 2009, 222-227)

3. [10Tang]: Correlation between thermodynamics and glass forming ability in the Al-Ce-Ni system (Intermetallics 18, 2010, 900-906)
After a thermodynamic modeling, 10 invariant reactions in the Al-rich corner have been computed by [10Tang]. They confirmed some of them by DTA experiments.

- E1: $L \rightarrow Al + Ce_3Al_{11} + NiAl_3$ (628.2°C)
- U1: $L + Ce_4Ni_6Al_{23} \rightarrow Ce_3Al_{11} + NiAl_3$ (735.7°C)
- U2: $L + Ni_2Al_3 \rightarrow Ce_4Ni_6Al_{23} + NiAl_3$ (843.0°C)
- U3: $L + CeNiAl_4 \rightarrow Ce_4Ni_6Al_{23} + Ce_3Al_{11}$ (896.5°C)
- U4: $L + CeNi_2Al_5 \rightarrow Ce_4Ni_6Al_{23} + Ni_2Al_3$ (901.1°C)
- P1: $L + CeNiAl_4 + CeNi_2Al_5 \rightarrow Ce_4Ni_6Al_{23}$ (998.2°C)
- U5: $L + CeAl_4 \rightarrow L + Ce_3Al_{11}$ (1019.4°C)
- U6: $L + \beta CeAl_3 \rightarrow CeNiAl_4 + CeAl_4$ (1104.7°C)
- U7: $L + CeAl_2 \rightarrow \beta CeAl_3 + CeNiAl_4$ (1167.6°C)
- P2: $L + CeAl_4 + CeAl_2 \rightarrow \beta CeAl_3$ (1191.9°C)
## Binary and ternary phases in the Al-rich part for the relevant phase diagrams

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition / at.%</th>
<th>Pearson symbol - type structure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce</td>
<td>Ni</td>
</tr>
<tr>
<td>Ce₃Al₁₁</td>
<td>22.4</td>
<td>-</td>
</tr>
<tr>
<td>α-CeAl₃</td>
<td>25.0</td>
<td>-</td>
</tr>
<tr>
<td>CeAl₂</td>
<td>33.3</td>
<td>-</td>
</tr>
<tr>
<td>Al₃Ni</td>
<td>-</td>
<td>25.0</td>
</tr>
<tr>
<td>Al₃Ni₂</td>
<td>-</td>
<td>40.0</td>
</tr>
<tr>
<td>Ce₄Ni₆Al₂₃</td>
<td>12.1</td>
<td>18.2</td>
</tr>
<tr>
<td>CeNiAl₄</td>
<td>16.7</td>
<td>16.7</td>
</tr>
<tr>
<td>CeNi₂Al₅</td>
<td>12.5</td>
<td>25.0</td>
</tr>
<tr>
<td>“Ce₁₂.₁Ni₂₈.₁Al₅₉.₈”</td>
<td>12.1</td>
<td>28.1</td>
</tr>
</tbody>
</table>

In [99Belov] the existence of a ternary eutectic reaction (L → Al + NiAl₃ + CeAl₄ *) with a global composition Ce₂.₆Ni₂.₆Al₉₄.₈ and a $T_E$ = 627°C has been reported.
Two recent publications about the Sm-Ni-Al system:

1. [08Delsante]: Phase relations of the Sm–Ni–Al ternary system at 500 °C in the 40–100 at.% Al region; (Intermetallics, 16 (11-12), 2008, 1250-1257)

2. [09Delsante]: Synthesis and Structural Characterization of Ternary Compounds Belonging to the Series $RE_{2+m}Ni_{4+m}Al_{15+4m}$ ($RE$ rare earth metal); (Z. Anorg. Allg. Chem., 635, 2009, 365-368)
E₁: \( L \rightarrow Al + Sm_{3}Al_{11} + Sm_{4}Ni_{6}Al_{23} \)  
\( (Sm_{2.5}Ni_{2.5}Al_{95}) \)

E₂: \( L \rightarrow Al + NiAl_{3} + Sm_{4}Ni_{6}Al_{23} \)  
\( (Sm_{1}Ni_{2}Al_{97}) \)

Isothermal section at 500°C
### Binary and ternary phases in the Al-rich part for the relevant phase diagrams

<table>
<thead>
<tr>
<th>Phase / T range (°C)</th>
<th>Composition / at.%</th>
<th>Pearson symbol - type structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>SmAl</td>
<td>Sm 50.0 Ni - Al 50.0</td>
<td>oP16-ErAl</td>
</tr>
<tr>
<td>SmAl₃</td>
<td>Sm 25.0 Ni - Al 75.0</td>
<td>hP8-Ni₃Sn</td>
</tr>
<tr>
<td>SmAl₂</td>
<td>Sm 33.3 Ni - Al 66.7</td>
<td>cF24-Cu₂Mg</td>
</tr>
<tr>
<td>AlNi</td>
<td>- 50.0 Ni 50.0</td>
<td>cP2-CsCl</td>
</tr>
<tr>
<td>Al₃Ni</td>
<td>- 25.0 Ni 75.0</td>
<td>cP4-Cu₃Au</td>
</tr>
<tr>
<td>Al₃Ni₂</td>
<td>- 40.0 Ni 60.0</td>
<td>hP5-Al₃Ni₂</td>
</tr>
<tr>
<td>Sm₃Ni₅Al₁₉</td>
<td>Sm 11.1 Ni 18.5 Al 70.4</td>
<td>oS108-Gd₃Ni₅Al₁₉ (stable only at 800°C)</td>
</tr>
<tr>
<td>Sm₄Ni₆Al₂₃</td>
<td>Sm 12.1 Ni 18.2 Al 69.7</td>
<td>mS66-Y₄Ni₆Al₂₃</td>
</tr>
<tr>
<td>SmNiAl₄</td>
<td>Sm 16.7 Ni 16.7 Al 66.6</td>
<td>oC24-YNiAl₄</td>
</tr>
<tr>
<td>SmNiAl₃</td>
<td>Sm 20.0 Ni 20.0 Al 60.0</td>
<td>oP20-YNiAl₃</td>
</tr>
<tr>
<td>SmNiAl₂</td>
<td>Sm 25.0 Ni 25.0 Al 50.0</td>
<td>oS16-CuMgAl₂</td>
</tr>
<tr>
<td>SmNi₂Al₃</td>
<td>Sm 16.7 Ni 33.3 Al 50.0</td>
<td>hP18-HoNi2.6Ga2.4</td>
</tr>
</tbody>
</table>
Experimental techniques

Pieces of the elements in pure Ar atmosphere
Synthesis in alumina crucibles by induction melting
Annealing for 10-15 days at 800°C
Quenching in ice-water

ISOTHERMAL SECTION INVESTIGATIONS

CHARACTERIZATION OF THE ALLOYS

LOM SEM EPMA

XRD

Differential Scanning Calorimetry and Thermal Analysis were also performed on some Ce-Ni-Al alloys
Ce-Ni-Al system: 11 alloys in the composition range 70 - 100 at.% Al have been synthesized and completely characterized.

Sm-Ni-Al system: 19 alloys in the composition range 55 – 100 at.% Al have been synthesized and completely characterized.
Results
Ce-Ni-Al: isothermal section at 800°C

Grey phase: NiAl$_3$
White phase: Ce$_3$Al$_{11}$
liquidus (ternary eutectic morphology)

Composition and crystal structures of the ternary phases Ce$_4$Ni$_6$Al$_{23}$ (mS66-Y$_4$Ni$_6$Al$_{23}$, CeNiAl$_4$ (oS24-YNiAl$_4$) were confirmed

For the Ce$_3$Al$_{11}$ a Ni solubility of ~2 at.% was observed.

The previously established phase relationships have been confirmed
BSE micrograph of a Ce$_{2.5}$Ni$_{3.0}$Al$_{94.5}$ sample: ternary eutectic morphology

The microstructure of the ternary eutectic is greatly affected by the solidification.

$T_E = 622^\circ C$
measured by DSC
The **experimental results** by DTA analysis confirmed the **calculated temperatures** for the invariant reactions reported by [10Tang], with a good agreement for U₃ and P₁

U₁: \( L + Ce₄Ni₆Al₂₃ \rightarrow Ce₃Al₁₁ + NiAl₃ \)  
\[ 700°C \quad [736°C] \]

U₃: \( L + CeNiAl₄ \rightarrow Ce₄Ni₆Al₂₃ + Ce₃Al₁₁ \)  
\[ 896°C \quad [896.5°C] \]

P₁: \( L + CeNiAl₄ + CeNi₂Al₅ \rightarrow Ce₄Ni₆Al₂₃ \)  
\[ 990°C \quad [998°C] \]
Sm-Ni-Al: isothermal section at 800°C

1. Sm₄Ni₆Al₂₃
2. Sm₃Ni₅Al₁₉
3. SmNiAl₄
4. SmNiAl₃
5. SmNiAl₂
6. SmNi₂Al₃
7. "Sm₁₃Ni₃₀Al₅₇"

Bright phase: SmAl₃
Grey phase: Sm₄Ni₆Al₂₃
Liquidus: SmAl₃

Light grey phase: SmNiAl₂

Grey phase: NiAl
Light grey phase: Ni₂Al₃

Dark Grey phase: SmNi₂Al₃

Bright phase: SmAl₂

Grey phase: NiAl
Light grey phase: SmNiAl₄
- The existence of the $\text{Sm}_4\text{Ni}_6\text{Al}_{23}$, $\text{SmNiAl}_4$, $\text{SmNiAl}_3$, $\text{SmNiAl}_2$ and $\text{SmNi}_2\text{Al}_3$ ternary phases previously reported for the isothermal section at 500°C were confirmed.

- The existence of the $\text{Sm}_3\text{Ni}_5\text{Al}_{19}$ in samples annealed at 800°C was also confirmed.

- A new phase with a composition $\sim\text{Sm}_{13}\text{Ni}_{30}\text{Al}_{57}$ was found.

- The relationships between binary and ternary phases have been proposed.
Ce-Ni-Al and Sm-Ni-Al systems: Isothermal sections at 800°C

Different behaviour of R-Ni-Al systems containing Ce or Sm

But, the phase reported by [08Tang] to exist at 800°C with an unknown structure and a composition ~Ce$_{12.1}$Ni$_{28.1}$Al$_{59.8}$ can be the same observed by us with a composition ~ Sm$_{13}$Ni$_{30}$Al$_{57}$
Conclusions -1

- Composition and crystal structures of the ternary phases Ce₄Ni₆Al₂₃, CeNiAl₄ were confirmed

- For the Ce₃Al₁₁ a Ni solubility of ~2 at.% was observed.

- The previously established phase relationships have been confirmed

- Temperature of several invariant reactions have been determined by DSC and DTA analysis
Conclusions -2

- The existence of the ternary phases Sm$_4$Ni$_6$Al$_{23}$, SmNiAl$_4$, SmNiAl$_3$, SmNiAl$_2$ and SmNi$_2$Al$_3$ previously reported for the isothermal section at 500°C were confirmed. The existence of the Sm$_3$Ni$_5$Al$_{19}$ in samples annealed at 800°C was also confirmed.

- A new phase with a composition ~Sm$_{13}$Ni$_{30}$Al$_{57}$ was found. A structural investigation is still needed.

- The relationships between binary and ternary phases have been proposed.

- The differences between the relationships occurring at 500°C and 800°C have been highlighted.

- Similarities and differences in the formation of ternary phases and in the established phase relationships for the Ce-Ni-Al and Sm-Ni-Al systems have been underlined.
THANK YOU FOR YOUR ATTENTION
$\text{Al}_{15+4m}\text{Ni}_{4+m}\text{R}_{2+m}$ structure series

$\text{R}_4\text{Ni}_6\text{Al}_{23}$
$\text{R} = \text{Y, Sm, Gd, Yb}$

$\text{R} = \text{heavy rare earths}$

$\text{R}_3\text{Ni}_5\text{Al}_{19}$
$\text{R} = \text{Y, Gd, Dy, Er}$

$\text{RNi}_3\text{Al}_9$
$\text{R} = \text{Gd}$

<table>
<thead>
<tr>
<th>Phase</th>
<th>at% R</th>
<th>at% Ni</th>
<th>at% Al</th>
<th>structure type</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{R}_3\text{Ni}<em>5\text{Al}</em>{19}$</td>
<td>11.11</td>
<td>18.52</td>
<td>70.37</td>
<td>oS108- $\text{Gd}_3\text{Ni}<em>5\text{Al}</em>{19}$</td>
</tr>
<tr>
<td>$\text{R}_4\text{Ni}<em>6\text{Al}</em>{23}$</td>
<td>12.12</td>
<td>18.18</td>
<td>69.7</td>
<td>mS66- $\text{Y}_4\text{Ni}<em>6\text{Al}</em>{23}$</td>
</tr>
<tr>
<td>$\text{RNi}_3\text{Al}_9$</td>
<td>7.69</td>
<td>23.08</td>
<td>69.23</td>
<td>hR78- $\text{ErNi}_3\text{Al}_9$</td>
</tr>
</tbody>
</table>
Bright phase: $\text{Sm}_3\text{Ni}_5\text{Al}_{19}$
Grey phase: $\text{Ni}_3\text{Al}_3$
liquidus

Bright phase: $\text{SmNiAl}_4$
Dark Grey phase: “new phase”
Grey phase: $\text{SmNiAl}_3$