高温酸化アルミナ皮膜の生成・相変態におよぼす種々の因子

—初期酸化皮膜から安定アルミナ皮膜への遷移—

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Protection of Heat-resistant Alloys Against High-Temperature Oxidation and Corrosion

Higher Temperature
Oxidizing, Corrosive atmospheres

1. Compact, Higher thermo-dynamical Stability
2. Good adhesion to substrate
3. Rapid formation, maintained for longer time

Cr$_2$O$_3$, Al$_2$O$_3$, and SiO$_2$

Steam turbines
Boiler tubes
Chemical plants

Gas turbines
Jet engines
Rocket engines
Growth of Metastable and $\alpha$-$\text{Al}_2\text{O}_3$ Scale

Ni-22Al-30Pt-Hf in air at $1150^\circ\text{C}$

Number of 1h cycles

Weight change, mg/cm$^2$

0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8

0
200
400
600
800
1000

metastable $\text{Al}_2\text{O}_3$

$\alpha$-$\text{Al}_2\text{O}_3$
Typical Forms Thermally Grown Alumina

\[ \gamma-\text{Al}_2\text{O}_3 \] (Cubic)

\[ \theta-\text{Al}_2\text{O}_3 \] (Monoclinic)

\[ \alpha-\text{Al}_2\text{O}_3 \] (Corundum)

Alloy composition
Atmosphere
Temperature
TTT Diagram of Thermally Grown Alumina

Growth rates of metastable and $\alpha$-$\text{Al}_2\text{O}_3$ scales

$\frac{k_p}{(\text{g}^2/\text{cm}^4/\text{s})}$ vs. temperature ($^\circ\text{C}$)

- $\alpha$-$\text{Al}_2\text{O}_3$ on NiAl
- $\theta$-$\text{Al}_2\text{O}_3$ on NiAl
- $\theta$-$\text{Al}_2\text{O}_3$ on FeAl
- $\gamma$-$\text{Al}_2\text{O}_3$ on NiAl
Effect(s) of Fe Deposit on the Phase Transformation to $\alpha$-$\text{Al}_2\text{O}_3$

Fe deposit

Fe deposited area

$900^\circ\text{C}$ for 10h in air

$\beta$-NiAl substrate

$\alpha$-$\text{Al}_2\text{O}_3$

metastable-$\text{Al}_2\text{O}_3$

Metal Coating Dependence on Metastable $\text{Al}_2\text{O}_3$ Formation

![Graph showing the mass gain (mg/cm$^2$) over time (h) for different metal coatings at 900°C.]

- **Ni coating**
- **Fe50Al**
- **Cr coating**
- **Fe coating**

Metal Coating Dependence on Metastable $\text{Al}_2\text{O}_3$ Formation

Ni coating

Fe coating

Fe-50Al

Cr coating

Fe50Al

Non coating

Fe-Al

$\theta$-$\text{Al}_2\text{O}_3$

$\alpha$-$\text{Al}_2\text{O}_3$

Fe-Al

Purpose of the Study

Clarify the effect of various elements on the transformation behavior of $\text{Al}_2\text{O}_3$ scale during HT oxidation by in-situ HT X-ray diffraction study by means of synchrotron radiation.
Experimental Setup for In-situ Measurement

- X-ray beam
  - Energy: 12.4 keV, $\lambda=1\text{Å}$
  - Heating rate: 10-100°C/min

Diagram showing:
- Storage ring
- X-ray beam
- PILATUS 2D detector
- Sample
- Thermocouple
- Heating stage
Experimental Setup for *In-situ* Measurement
Experimental Procedures

Effect of Fe on the Transformation of Al2O3 Scale

Alloys: Fe-45~52at%Al (FeAl)

Coatings: Fe ~100nm (PVD)

Oxidation: in air, air + 7.6H₂O
in lowPₐ₀₂ = 1.8 x 10⁻¹³ atm (Ar-0.9H₂-7.6H₂O)
(FeO/Fe₃O₄, 1.2 x 10⁻¹² atm)
at 1000 ~ 1100°C

Heating and cooling rate: 50°C/min for heating
about 300°C/min for cooling

Oxidation time: 1 or 4h
Evolution of Oxide Scale during the HT Oxidation

Non-coated Fe-Al at 1000°C for 4h

θ-Al₂O₃

α-Al₂O₃

379°C

867°C

948°C

997°C

999°C

999°C

999°C

999°C

999°C

589°C

32°C
Change in Intensities of Different Al$_2$O$_3$ Phases

![Graph showing the change in intensities of different Al$_2$O$_3$ phases with oxidation time and temperature.](image)

- Temperature, °C
- Oxidation time, min
- Intensity, a.u.

<table>
<thead>
<tr>
<th>Phase</th>
<th>(002)</th>
<th>(113)</th>
<th>(104)</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ-Al$_2$O$_3$</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>α-Al$_2$O$_3$</td>
<td></td>
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</tbody>
</table>

Heating:

- θ-Al$_2$O$_3$ (002)
- α-Al$_2$O$_3$ (104)
Change in Lattice Spacing of $\alpha$-$\text{Al}_2\text{O}_3$

Lattice spacing, Å

Temperature, °C

Oxidation time, min

$d=2.5724$: Pure-$\text{Al}_2\text{O}_3$ at 1000°C
Evolution of Oxide Scale During the HT Oxidation

Fe-coated Fe-Al at 1000°C for 1h

Heating

Isothermal oxidation for 1h

Cooling

101°C
462°C
998°C
998°C
999°C
999°C
998°C
947°C
866°C
703°C
541°C
378°C
297°C

High-angle

Intensity, a.u.

α-Al₂O₃

Fe₂O₃

Fe₂O₃

Al₂O₃

R.T.

1000°C

500°C
Change in Lattice Spacing of Oxide Scale

Temperature, °C

Lattice spacing, Å

Change in Lattice Spacing of Oxide Scale

2.7214: Pure-Fe\(_2\)O\(_3\) at 800°C

2.7032: Al\(_2\)O\(_3\)-saturated Fe\(_2\)O\(_3\) at 1000°C

2.5795: Fe\(_2\)O\(_3\)-saturated Al\(_2\)O\(_3\) at 1000°C

2.5719: Pure-Al\(_2\)O\(_3\) at 1000°C

Oxidation time, min

Temperature, °C

Lattice spacing, Å

Oxidation time, min

Oxidation time, min

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Oxidation time, min
TEM Cross-section and EDS Analysis of α-Al₂O₃

**Fe-coated Fe-Al at 1000°C for 1h**

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Al</th>
<th>O</th>
<th>Solid Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42.0</td>
<td>7.1</td>
<td>50.9</td>
<td>14.5 mol%Al₂O₃</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>29.1</td>
<td>68.3</td>
<td>7.9 mol%Fe₂O₃</td>
</tr>
<tr>
<td>3</td>
<td>1.4</td>
<td>31.3</td>
<td>67.3</td>
<td>4.3 mol%Fe₂O₃</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>30.6</td>
<td>69.3</td>
<td>0.3 mol%Fe₂O₃</td>
</tr>
<tr>
<td>5</td>
<td>0.2</td>
<td>31.3</td>
<td>68.5</td>
<td>0.6 mol%Fe₂O₃</td>
</tr>
</tbody>
</table>

| 6 | 2.5  | 30.7| 66.8| 7.5 mol%Fe₂O₃ |
| 7 | 1.9  | 28.1| 70.1| 6.3 mol%Fe₂O₃ |
| 8 | 0.3  | 32.6| 67.1| 0.9 mol%Fe₂O₃ |
| 9 | 0.0  | 31.5| 58.5| 0 mol%Fe₂O₃  |
| 10| 0.2  | 32.9| 67.0| 0.6 mol%Fe₂O₃ |

| 11| 35.1 | 6.5 | 58.4| 15.6 mol%Al₂O₃|
| 12| 1.2  | 33.9| 64.9| 3.4 mol%Fe₂O₃ |
Effect of $P_{O_2}$ on the Transformation of $\text{Al}_2\text{O}_3$

*Bulk Fe-52Al oxidized in air, air+$\text{H}_2\text{O}$ or $\text{H}_2/\text{H}_2\text{O}$ at 1100°C*

![Graph showing the transformation of $\text{Al}_2\text{O}_3$ under different conditions.](Image)
Effect of H$_2$O and/or P$_{O2}$ on the Transformation to $\alpha$-Al$_2$O$_3$

Fe-50at%Al合金
1100°C

Oxidation time, min

Intensity, a.u.

$\theta$-Al$_2$O$_3$ → $\alpha$-Al$_2$O$_3$

Air+H$_2$O

$\theta$-Al$_2$O$_3$ → $\alpha$-Al$_2$O$_3$

H$_2$/H$_2$O

$\theta$-Al$_2$O$_3$ → $\alpha$-Al$_2$O$_3$

Air+H$_2$O
TEM Cross-sections of $\alpha$-$\text{Al}_2\text{O}_3$

*Bulk Fe-52Al at 1100°C for 1h (40min)*

- in air for 1h
- in air+$\text{H}_2\text{O}$ for 40min
- in $\text{H}_2$/H$_2\text{O}$ for 1h
Effect of $P_{O_2}$ on the Transformation of $\text{Al}_2\text{O}_3$

*Fe-coated Fe-52Al oxidized in air or $\text{H}_2/\text{H}_2\text{O}$ at 1100°C*

**Intensity, a.u.**

2θ, degree
TEM Cross-sections of $\alpha$-$\text{Al}_2\text{O}_3$

Fe-coated Fe-52Al at 1100°C for 1h (40min)

$\text{Fe}_2\text{O}_3$ is necessary to form $\alpha$-$\text{Al}_2\text{O}_3$ without metastable $\text{Al}_2\text{O}_3$ formation

in air for 1h

in $\text{H}_2$-$\text{H}_2\text{O}$ for 1h

400nm

$\alpha$-$\text{Al}_2\text{O}_3$
Modified Ternary Fe-Al-O System

Summary

Formation of $\alpha$-$A_2O_3$ from $Fe_2O_3$ was confirmed by in-situ measurement via synchrotron radiation.

Precipitation of $\alpha$-$Al_2O_3$ (sympathetic nucleation) occurred when $Fe$-coated alloy was oxidized in air.

In low $P_{O_2}$, Metastable $Al_2O_3$ formed and it’s transformation to $\alpha$-$Al_2O_3$ delayed.

Transformation to $\alpha$-$A_2O_3$ was delayed and/or metastable $\theta$-$Al_2O_3$ was stabilized:

- On the alloys with lower $Fe$ content.
- In the atmosphere with lower partial pressure of oxygen.

Lower $Fe$ content in the metastable $Al_2O_3$ delayed the transformation.